CODING FORM FOR SRC INDEXING

REVISED 10/15/86

Microfiche No.	GTS0514803
New Doc I.D.	86-870000693
Old Doc I.D.	
Date Produced	9/13/79
Date Recieved	
TSCA section	8D
Submitting Organization	RESEARCH INST FOR SAFETY ENG
Contractor	
Document Title	STACK EMISSION PART A EMITTED TOLUENE DIISOCYANATE GAS TREATMENT WITH ACTIVATED SLUDGE WITH ATTACHMENT
Chemical Category	TOLUENE DIISOCYANATE (1321-38-6)

III Project No: FE-E-15-II
Date of Report: Sept.13,1979

COMPLETE REPORT

TO

THE INTERNATIONAL ISOCYANATE INSTITUTE

BY

RESEARCH INSTITUTE FOR SAFETY ENGINEERING

5-6,Ginza 8-Chome,Chuo-ku,Tokyo,104,Japan

TITLE

STACK EMISSION, PART A,

EMITTED TDI GAS TREATMENT WITH ACTIVATED SLUDGE

Author

Shukuji Asakura, Ph.D

Associate Professor

Department of Safety Engineering

Yokohama National University

LIST OF CONTENTS

CONTENTS PAGE

1. Abstract 1
2. Introduction 2
3. Culture of activated sludge with aniline 6
   3.1. Experimental 6
   3.2. Results 7
   3.3. Discussions 9
4. Culture of activated sludge with the reaction product of TDI with water. 19
   4.1 Experimental 19
   4.2 Results for the culture of the aniline acclimated sludge with r.p.-TDI (Culture I) 19
   4.3 Discussions for the culture of the aniline acclimated sludge with r.p.-TDI (Culture I) 21
   4.4 Results for the culture of the CSL acclimated sludge with r.p.-TDI (Culture II) 22
   4.5 Discussion for the culture of the CSL acclimated sludge with r.p.-TDI (Culture II) 23
5. Culture of activated sludge with tolylene diamine 44
   5.1 Introduction 44
   5.2 Experimental 44
   5.3 Results for the culture of the aniline acclimated sludge with 2, 6 TDA (Culture I) 45
   5.4 Discussions for culture of the aniline acclimated sludge with 2, 6 TDA (Culture I) 47
   5.5 Results for the culture of the CSL acclimated sludge with 2, 6 TDA (Culture II) 49
   5.6 Discussions for the culture of the CSL acclimated sludge with 2, 6 TDA (Culture II) 50
6. Culture of activated sludge with triethylenediamine 63

6.1 Introduction 63

6.2 Experimental 63

6.3 Results for the culture of aniline acclimated sludge with triethylenediamine (Culture I) 63

6.4 Discussions for the culture of aniline acclimated sludge with triethylendiamine (Culture I) 64

6.5 Results for the culture of CSL acclimated sludge with triethylendiamine (Culture II) 65

6.6 Discussions for the culture of CSL acclimated sludge with triethylendiamine (Culture II) 67

7. Culture of activated sludge with N,N,N'N' tetramethyl-diamino diethyl ether 80

7.1 Introduction 80

7.2 Experimental 80

7.3 Results 80

7.4 Discussions 82

INDEX OF FIGURES

Fig. 3-1. MLSS of activated sludge during culture with aniline

Fig. 3-2. pH change of activated sludge during culture with aniline.

Fig. 3-3. SVI of activated sludge during culture with aniline

Fig. 3-4. Removed aniline

Fig. 3-5. Removal efficiency of aniline

Fig. 3-6. Respiration rate before addition of aniline (r.r.1)

Fig. 3-7. Respiration rate after addition of aniline (r.r.2) (30 minutes after addition of aniline)

Fig. 3-8. Biological phase

fig. 4-1. PH change for culture (I) (1)

Fig. 4-2. PH change for culture (I) (2)

Fig. 4-2. MLSS for culture (I) (1)

Fig. 4-2. MLSS for culture (I) (2)

Fig. 4-3. SVI for culture (I) (1)

Fig. 4-3. SVI for culture (I) (2)

Fig. 4-4. COD of top water for culture (I) (1)

Fig. 4-4. COD of top water for culture (I) (2)

Fig. 4-5. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I) (1)

Fig. 4-5. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I) (2)

Fig. 4-6. PH change for culture (II) (1)

Fig. 4-6. PH change for culture (II) (2)

Fig. 4-7. MLSS for culture (II) (1)

Fig. 4-7. MLSS for culture (II) (2)

Fig. 4-8. SVI for culture (II) (1)

Fig. 4-8. SVI for culture (II) (2)

Fig. 4-9. COD of top water for culture (II) (1)

Fig. 4-9. COD of top water for culture (II) (2)

Fig. 4-10. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II) (1)

Fig. 4-10. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II) (2)

Fig. 5-1. PH change for culture (I)

Fig. 5-2. MLSS for culture (I)

Fig. 5-3. SVI for culture (I)

Fig. 5-4. COD of top water for culture (I)

Fig. 5-5. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I)

Fig. 5-6. Treatment efficiency for culture (I)

Fig. 5-7. PH change for culture (II)

Fig. 5-8. MLSS for culture (II)

Fig. 5-9. SVI for culture (II)

Fig. 5-10. COD of top water for culture (II)

Fig. 5-11. Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II)

Fig. 6-1. PH change for culture (I)

Fig. 6-2. MLSS for culture (I)

Fig. 6-3. SVI for culture (I)

Fig. 6-4. COD of top water for culture (I)

Fig. 6-5. Respiratopm rates befpre (r.r.1) and after (r.r.2) the addition of nutritions for culture (I)

Fig. 6-6. PH change for culture (II)

Fig. 6-7. MLSS for culture (II)

Fig. 6-8. MLSS versus time for culture (II)

Fig. 6-9. COD of top water for culture (II)

Fig. 6-10. SVI and SV30 for culture (II)

Fig. 6-11. Respiration rate for culture (II)

Fig. 7-1. PH change of activated sludge during culture with A-1

Fig. 7-2. MLSS of activated sludge during culture with A-1

Fig. 7-3. SVI of activated during culture with A-1

Fig. 7-4. COD of top water during culture with A-1

Fig. 7-5. Respiration rates before (r.r.1) and after (r.r.2) the addition of A-1

1. Abstract

Being continued from the research, III Project No. FE-E-15, the culture of activated sludge to the possible effluent from TDI related industry was studied.

The activated sludge was cultured with aniline, triethylendiamine, tolylendiamine, NNN'N' tetramethyl-diamino-diethyl-ether, and the reaction product of TDI with water in the batch process.

A half amount of total top water was replaced with the buffer solution which consisted of K_2HPO_4, KH_2PO_4, $Na_2HPO_4 \cdot 12H_2O$, NH_4Cl, $MgSO_4$, $CaCl_2$, and $FeCl_3 \cdot 6H_2O$.

Chapter 3 described the acclimation with aniline. The activated sludge originated from CSL (synthetic waste water) culture could be acclimated with aniline in about a month. The acclimated sludge could treat aniline with excellent efficiency even at relatively high loading.

In Chapter 4, the cultures of the activated sludges with the reaction product of TDI with water were attempted.

The sludges used were obtained from both CSL-culture and aniline-culture vessels.

The both experiments for 130 days did not show the possibility of metabolism and a slight inhibition of activity was observed.

Chapter 5 treated the acclimation of tolylene diamine which was a reaction product of TDI with water. The activated sludge originated from aniline culture did not loose its activity as long as the loading of tolylene diamine was less than 20 ppm - COD equivalent

However, the addition of tolylene daimine to the CSL-cultureed sludge gradually made it completely inactive even at the very low loading.

Thus, it might be suggested that the sludge was cultured with aniline to treat the possible effluent containing tolylendiamine.

In Chapter 6, the acclimation tests for triethylendiamine were mentioned.

For both aniline cultured and CSL cultured sludges triethylerdiamine was not harmful.

Though being not completely conclusive due to the limitation of cultural time, triethylendiamine seemed to be metabolized with aniline acclimated sludge.

For the CSL acclimated sludge, the contradictory results made it unable to obtain definite conclusion.

As described in Chapter 7, NNN'N'-tetramethyl-diamino-diethyl-ether showed the similar behaviours to those for the case of aniline.

It seemed to be evident that NNN'N' tetramethyl-diamino-diethyl -ether could be biologically treated.

2. Introduction

The general principle of activated sludge processes have been described in the previous report, III Project No. FE-E-15.

The present studies were forcused upon the acclimation and decomposition processes of the organic substances related to TDI industry with respect to activated sludges.

It would be preferable to review the similar studies conducted before.

Malaney [1)] found that aniline was metabolized with the microbes in the activated sludge and could be acclimated with it.

Malaney examined the biological oxidation of the phenylendiamines with the aniline-acclimated sludge.

As appearing in Fig. 2-1, oxygen up-take of phenylendiamine was lower than that of aniline.

Its difference between isomers of phenylendiamine was slight.

The introduction of NO_2-, SO_3-, and Cl- groupes to benzen ring of aniline decreased the biological degradability.

Baird [2)] studied the effect of phenol and its family on the activity of activated sludge.

When they were added to the sludge which was not acclimated with phenol, the oxygen up-take was inhibited very sensitively and vice versa. However, they were found to be decomposed even when they hindered the activity of the sludge.

Mckinney and coworkers [3)] performed the similar experiments and summarized their results as :

(1) Activated sludge could treat phenol and its family.

(2) Phenol and its family did not diminish the activity of activated sludge as long as their concentration were less than 500 ppm.

(3) Phenyls were oxidized mainly being controlled by the mass transfer rate of oxygen.

(4) Treatability of phenyls was dependent on their structure.

Kaneko and his coworker [4)] studied the effect of PCB on the activated sludge. PCB was difficult to oxidize biologically and was condensed in the sludge.

Navak and Kraus [5)] examined the decomposition of fatty acids of long chain with activated sludge. They did not deactivate the activity of sludge.

Their treatability was not influenced by the degree of saturation and the length of the chain.

Cox and Conway [6)] reported the biodegradation of polyethylenglycol up to 5000 molecules.

Po-Young [7)] and coworkers found the accumlation of nonhydrophilic phenyl compounds in the lipid.

Literature

(1) G.W. Malaney, J.W.P.C.F. 32 1300, (1960)

(2) R.B. Baird et al,
Archives of Environ. Contamination and Toxicology
2 165 (1974)

(3) R.E. Mckinney et al.
Sewage and Industrial Wastes 547 (1956)

(4) M. Kaneko et al.
Water Res. 10 157 (1976)

(5) J.T. Novak and D.L. Kraus
Water Res. 17 843 (1973)

(6) D.P. Cox and R.A. Conway
Int. Biodegradation Symp. (3rd) 835 (1976)

(7) Po-Young et al.
Environ. Health Perspective 10 (4) 269 (1975)

3. CUlture of activated sludge with aniline.

According to Malaney [1], the acclimation processes of some compound swhich included nitrogen were similar to those of aniline. At the same time, he found that a number of N-containing substances could become the substrates for the sludge when the aniline - acclimated sludge was cultured with them.

Therefore, the activated sludge cultured with simulated waste water was examined to be acclimated with aniline.

3.1 Experimental

The activated sludge subject to acclimation had been continuously cultured with corn steep liquor (simulated waste water) in the aeration vessel of 98 ℓ in volume which appeared in Fig. 2-17 of the preceeding report (III Project No. FE-E-15). The sludge thus cultured was ladled up into the smaller aeration vessel of about 30 ℓ and was cultured at the same conditions as above for four days.

Then, the addition of CSL (Corn Steep Liquor) was stopped and the sludge was aerated without feeding for three days. After the sludge went into endgeneous conditions, the aeration was stopped for a while to sediment the sludge and replace the top water of 9 ℓ with the buffer solution. This replacement has been done every day during the acclimation experiment. At the same time a certain amount of aniline was added. The buffer solution was prepared by mixing the solution A (60 mℓ), solution B, C, and D (20 mℓ each), and water (720 mℓ). The compositions of solutions were;

Solution A;	K_2HPO_4	21.75 g/ℓ
	KH_2PO_4	8.5 g/ℓ
	$Na_2HPO_4 \cdot 12H_2O$	44.6 g/ℓ

	NH_4Cl	1.7 g/ℓ
Solution B;	$MgSO_4 \cdot 7H_2O$	27.5 g/ℓ
Solution C;	$CaCl_2$ (anhydrous)	22.5 g/ℓ
Solution D;	$FeCl_3 \cdot 6H_2O$	0.25 g/ℓ

The temperature and the concentration of dissolved oxygen were maintained at about 25°C and 2 to 3 ppm, respectively. (The derivation of parameters was followed after the previous report presented to III).

esults

the following figures, the quantity of added aniline expressed in terms of COD concentration. Actually, total amount of COD was divided by the whole volume ludge solution and then shown in the figures.

SS

change in MLSS (Mixed Liquor Suspended Solid) ng culture appears in Fig. 3-1. he initial period of culture MLSS decreased from 3500 ppm to about 2000 ppm and then stayed constant around 2000 ppm for about 30 days. then, it started to increase up to 3500 ppm. ue around 3500 ppm was maintained after about of culture.

shows pH change of activated sludge during Maximum is observed around 40 days of After 45 days of culture, pH was attained value around 6.5.

3.2.3 SVI

SVI (Sludge Volume Index) increased gradually from 40 mℓ/g in the initial period and stayed at relatively high value between 15 and 40 days of culture (Fig. 3-3).
At the 45 days it decreased sharply to 30 mℓ/g and continued to decrease.

2.4 Removal efficiency of aniline

COD (Chemical Oxygen Demand) of top water was measured immediately before and after the addition of aniline. (Fig. 3-4). The difference of COD after the addition from that before the addition of next day corresponded to the amount of COD treated biologically.
The amount of treated COD is given in Fig. 3-4.
The removal efficiency was calculated and plotted in Fig. 3-5.
It exceeded 95% except the initial few days.

Respiration Rate

Fig. 3-6 gives the respiration rate before the addition of aniline. It was less than 10 mg O_2/g·MLSS·hr, which meant that the sludge was at the endgeneous condition. The respiration rate was measured at 30 minutes after the addition of aniline.
As seen in Fig. 3-7, in the initial 30 days it stayed at low value and then increased. This means that after 30 days culture the sludge responded sensitively to aniline.

iological Observations

rotozoans was observed by using the microscope of
) magnifications.

e results are given in Fig. 3-8.

this figure, the circles mean that protozoans
e observed more than an individual in the field
microscope vision, the triangles do that indivi-
l exsisted in the sludge but not always were found
the field of vision, and the crosses do that no
ividual was observed.

as found that protozoans were going to disappear
he time of culture proceeded.

ions

g to the results, the cultural interval seemed
vided to four periods.

t period was the initial 7 days, where MLSS
d and SVI increased.

d period was the following 20 days, where the
on proceeded and the biological phases were
changed.

eriod, the parameters were not stable.

period was the following 10 days, where MLSS
spiration response to the addition of aniline
abruptly.

period appeared after the culture of 45 days
e.

iod, the parameters were stable and the
llently treated aniline.

that the activated sludge was completely acclimated in the fourth period :

Since protozoans disappeared in the last period, the biological environment of the sludge acclimated with aniline was not preferable to them.

The following conclusion were obtained.

(1) The activated sludge which had been cultured with CSL could be acclimated with aniline.

(2) The treatability of aniline with acclimated sludge was excellent even at the relatively high load such as F/M = 0.3.

(3) The acclimated sludge was very stable.

(4) It took about 30 days to acclimate the sludge.

(5) The change in biological phase was observed with acclimation.

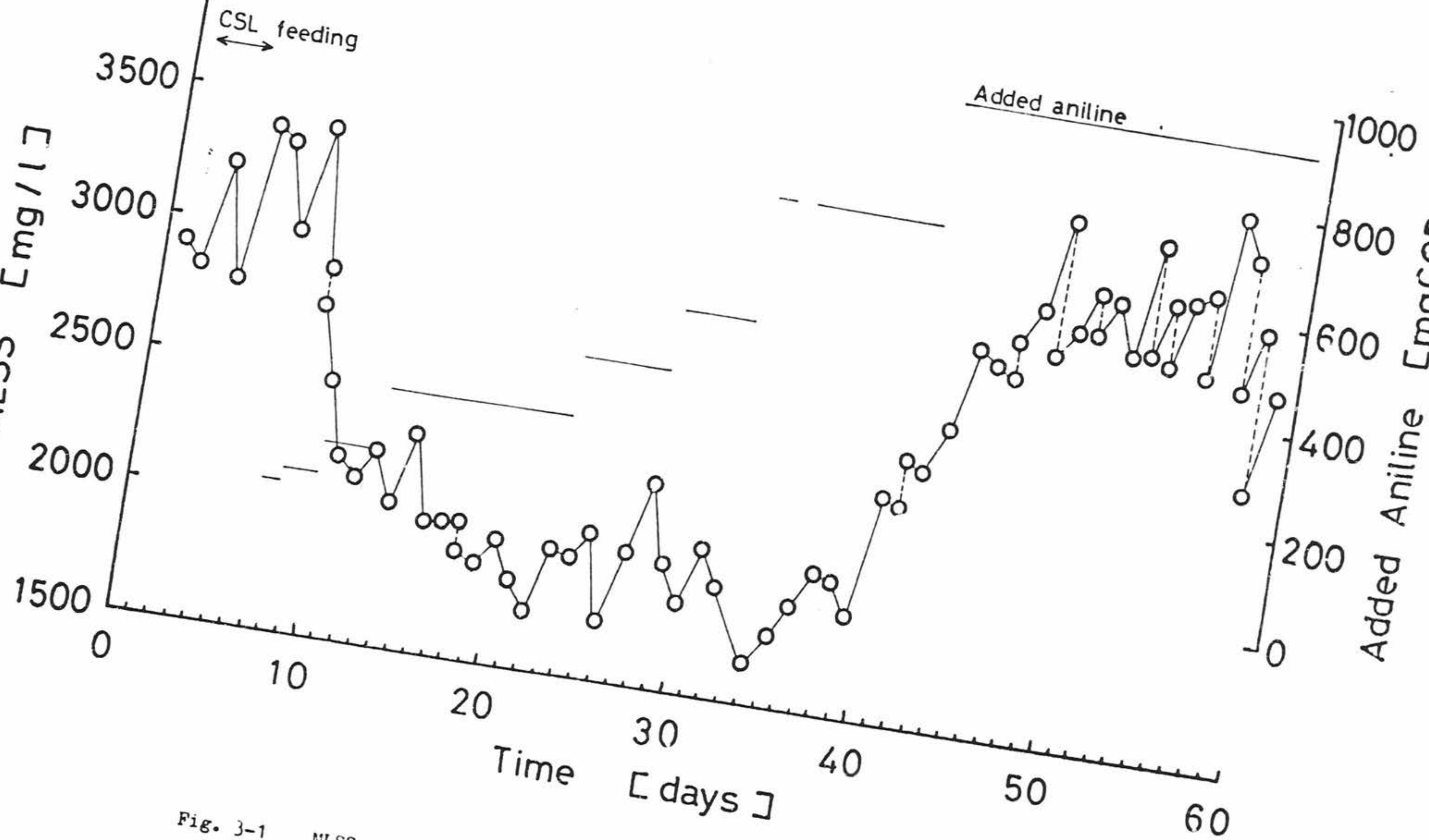


Fig. 3-1 MLSS of activated sludge during culture with amiline.

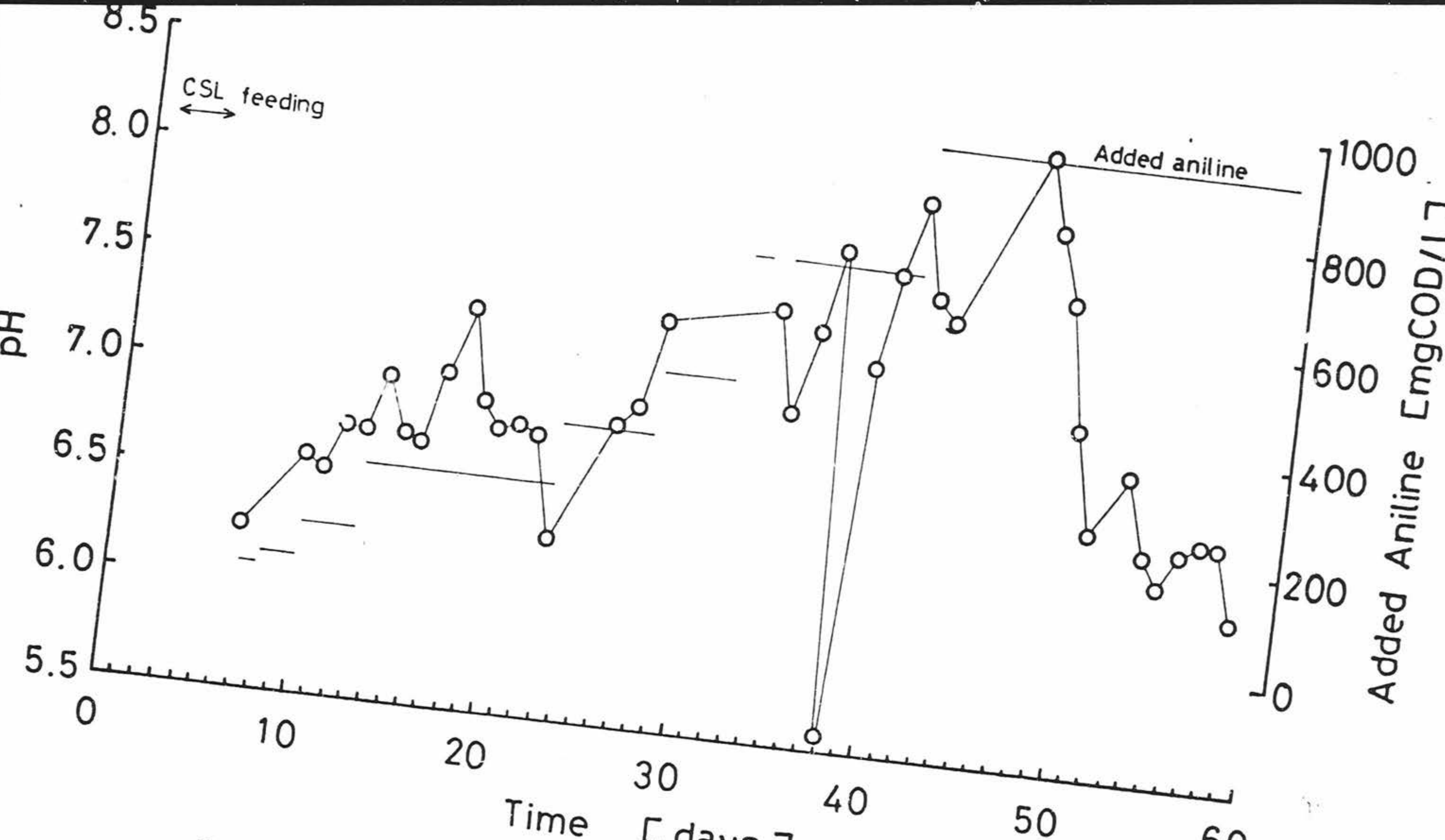


Fig. 3-2 pH change of activated sludge during culture with aniline.

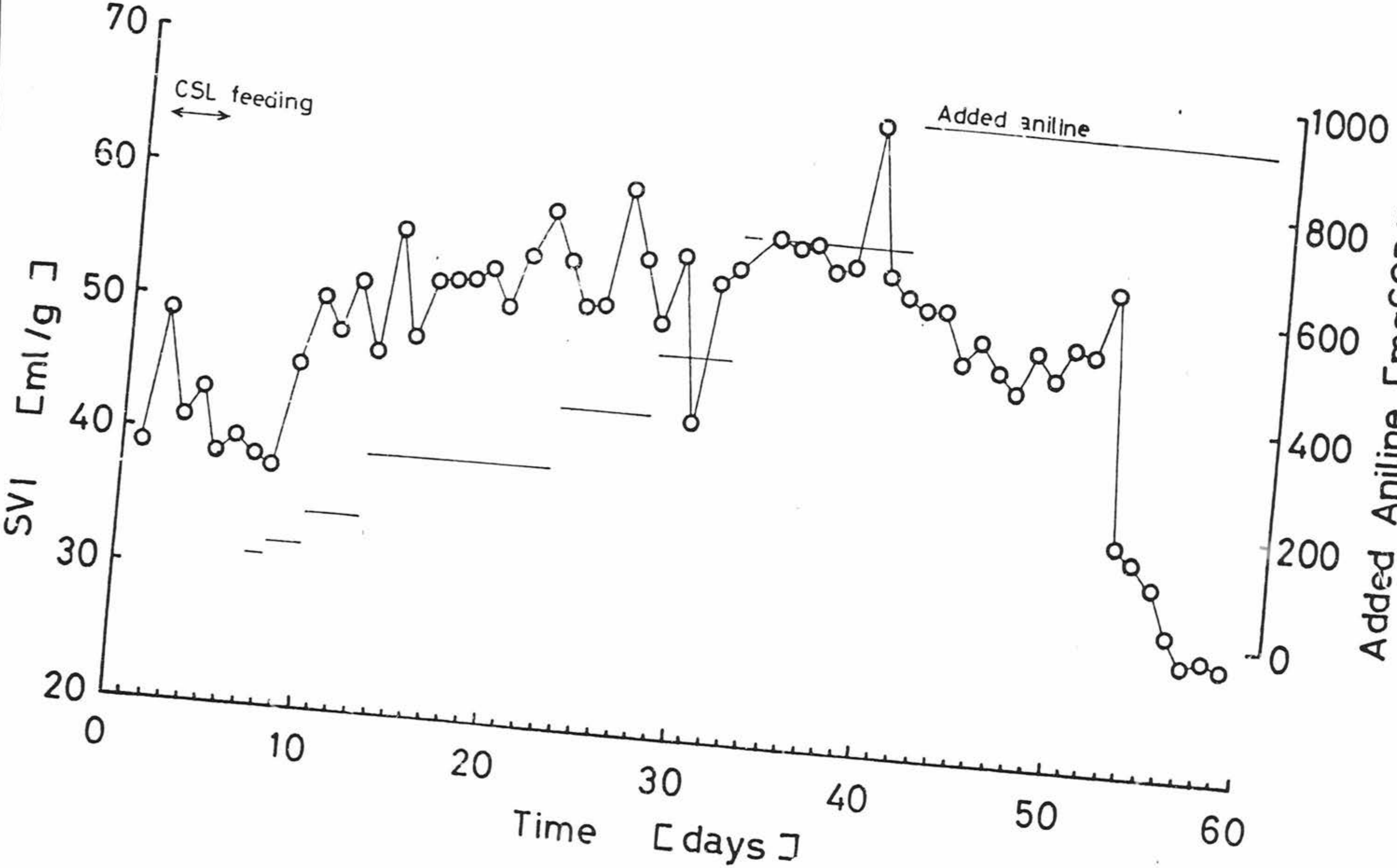


Fig. 3-3 SVI of activated sludge during culture with aniline.

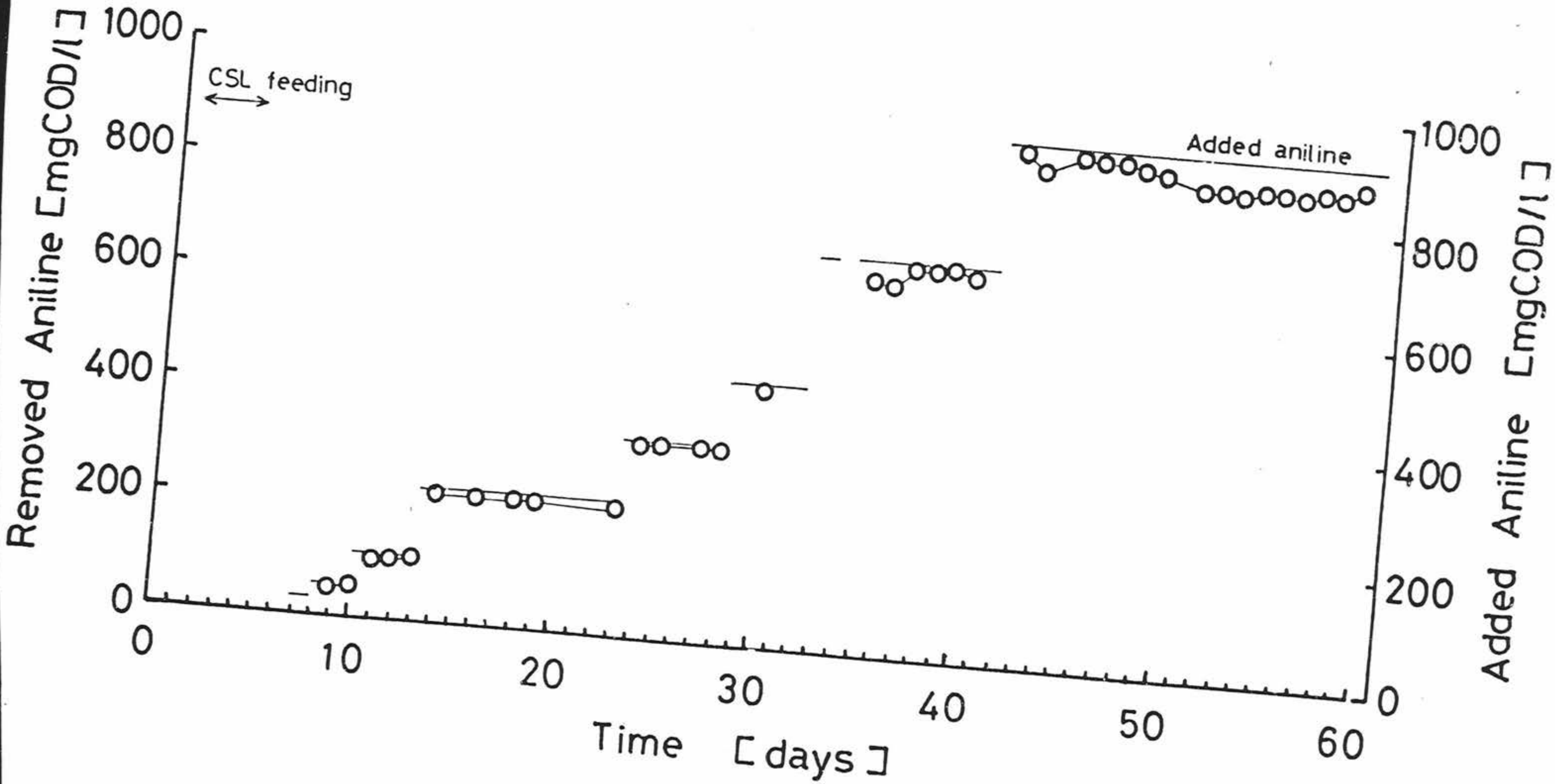


Fig. 3-4 Removed aniline.

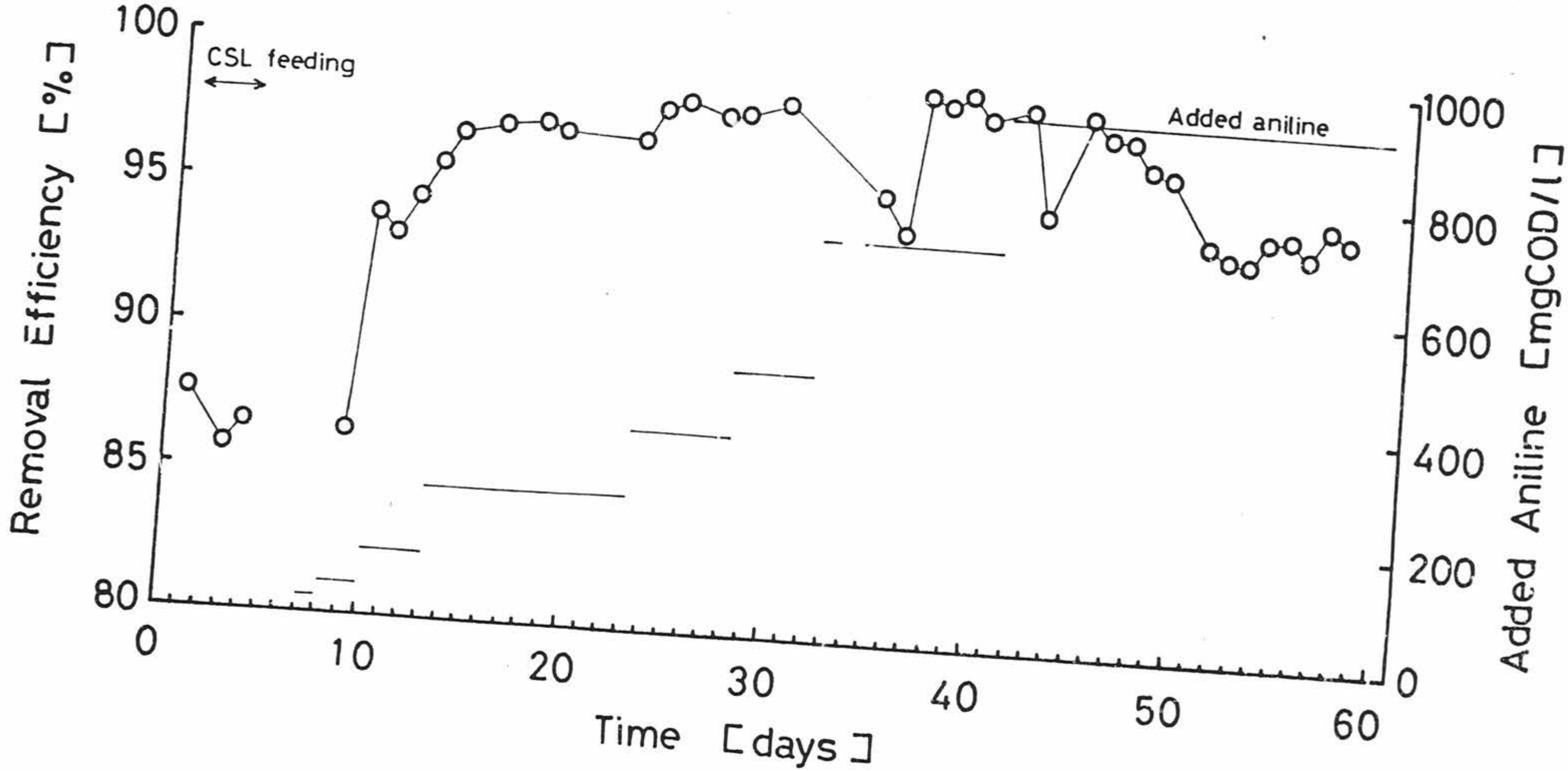


Fig. 3-5 Removal efficiency of aniline.

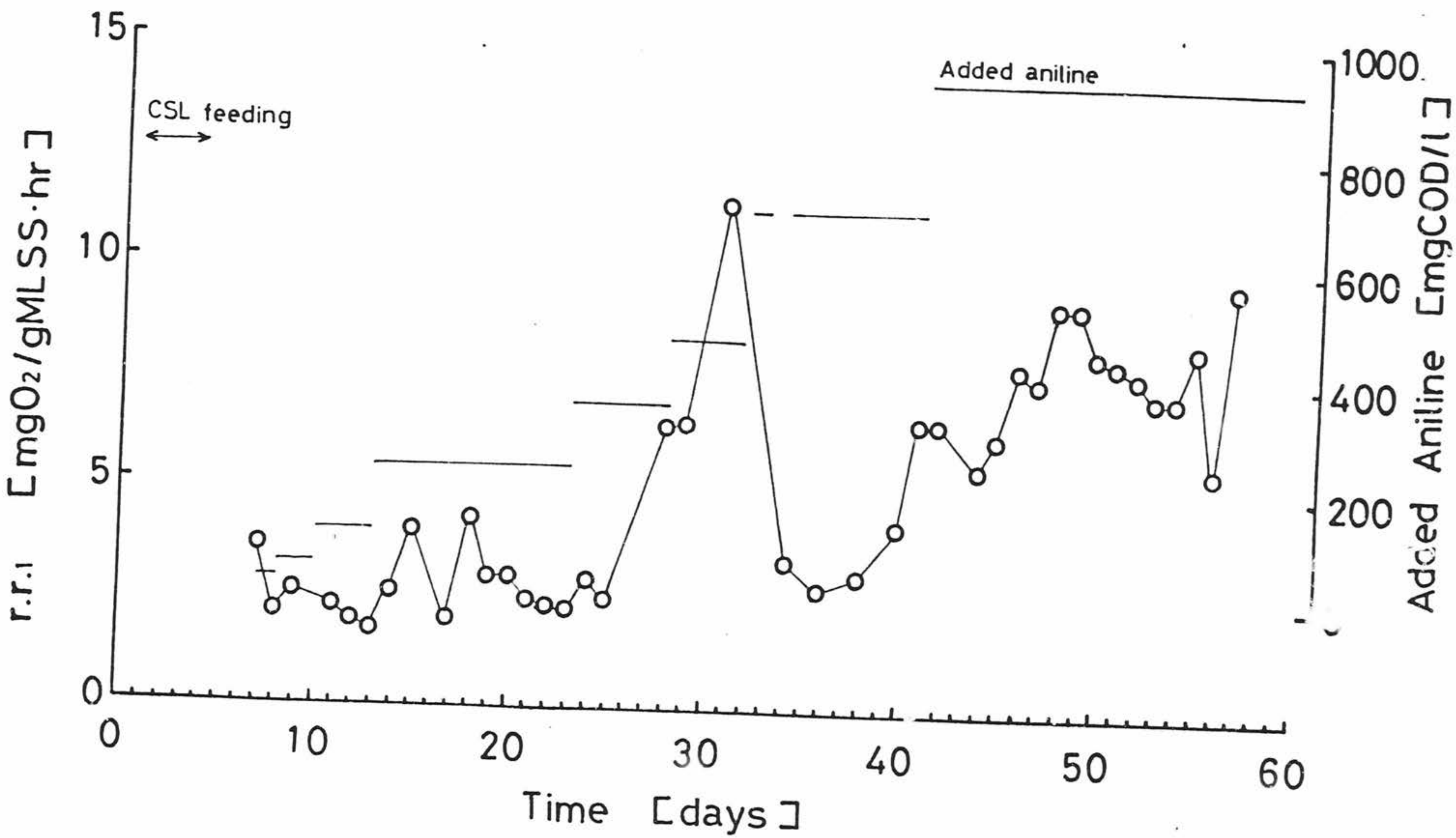


Fig. 3-6 Respiration rate before addition of aniline (r.r.1)

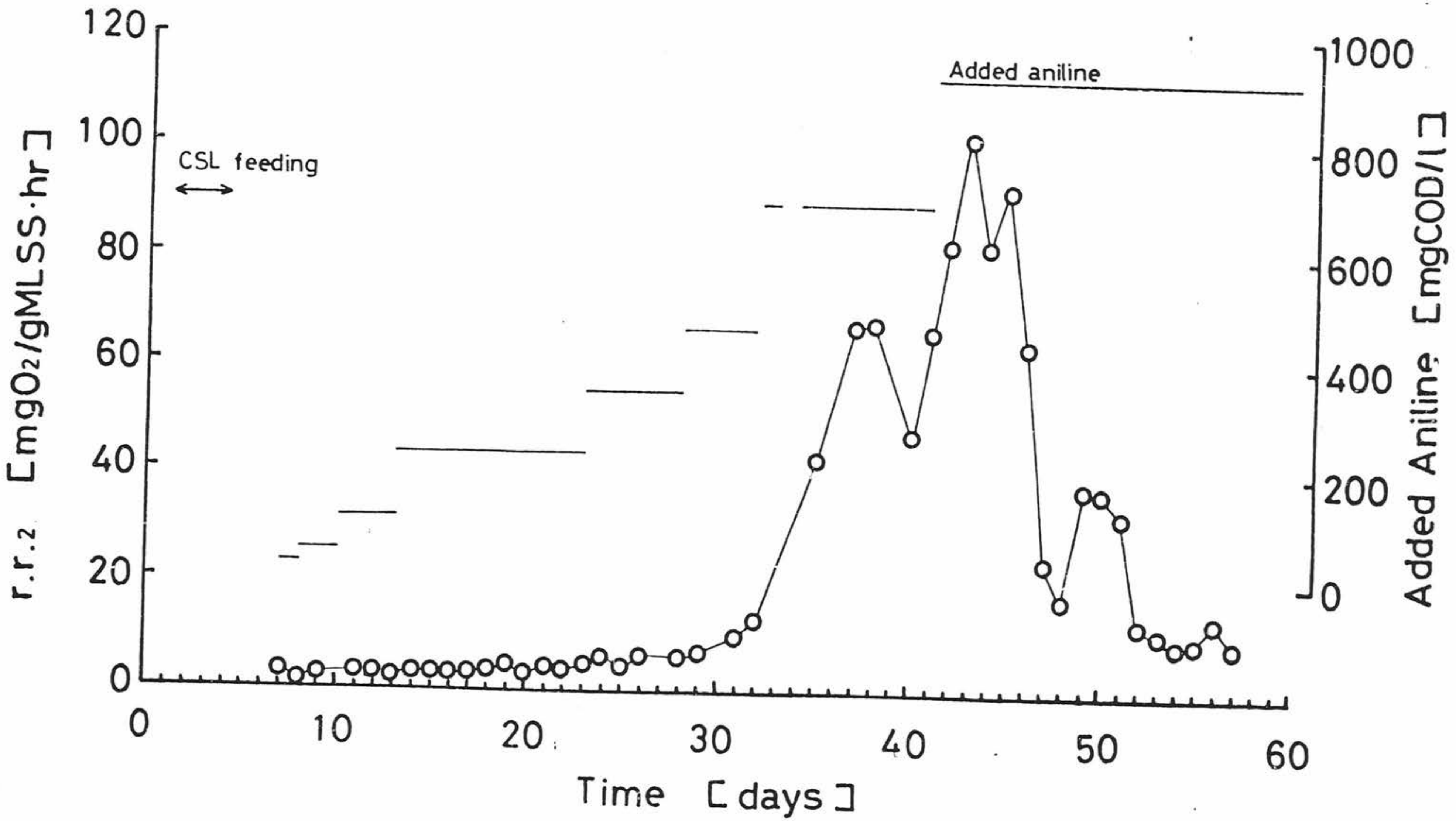


Fig. 3-7 Respiration rate after addition of aniline (r.r.2)

(30 minutes after addition of aniline)

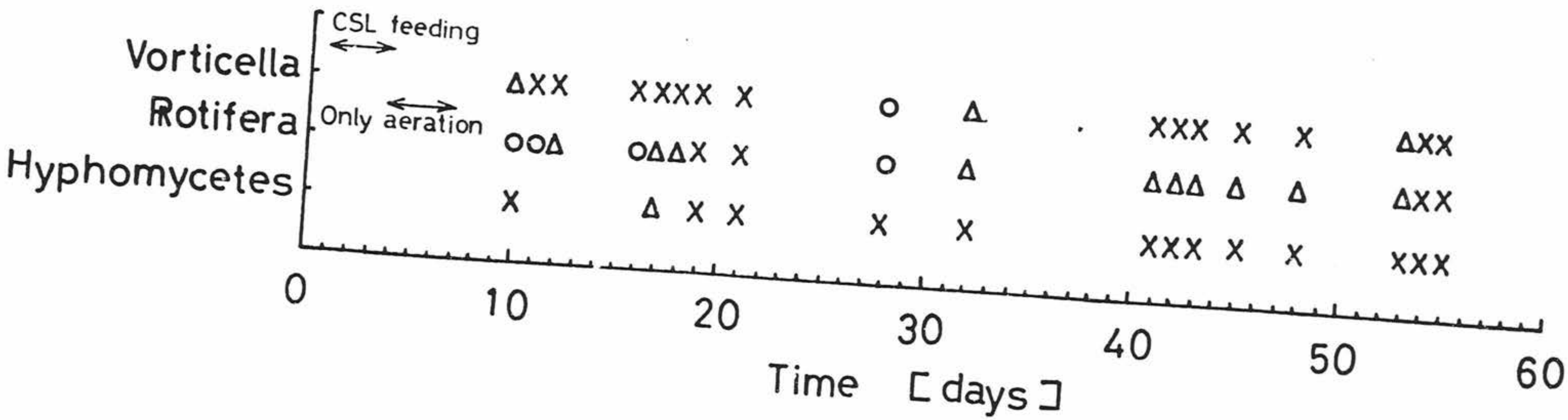


Fig. 3-8 Biological phase.

4. Culture of activated sludge with the reaction product of TDI with water.

4.1 Experimental

The two kinds of activated sludge were used for the culture test with the reaction product of TDI with water (r.p.-TDI).
They were the sludges cultured with aniline and CSL.
The procedure of culture was similar to that described in the preceeding chapter.
The sludges taken from the respective vessels were cultures with nutritions same as previous ones in the 25 ℓ vessels.
When the conditions of sludges were attained at the desired ones, the feeding of nutritions was stopped.
The sludges were aerated until they were completely endgeneous. Thereafter, the top water of 9 liters was replaced with the buffer solution of the same amount every day. The composition of buffer solution was same as that given in Chapter 3.
At the same time, certain amounts of nutrition and r.p.-TDI were added day by day. In the course of experiment, the nutritions such as aniline and CSL were fed along with r.p.-TDI. r.p.-TDI used in this experiment was prepared by mixing TDI and water within one minute before addition.
The concentrations of aniline, CSL, and r.p.-TDI were given in Figures. The value for r.p.-TDI was expressed by assuming that TDI was simply dissolved in the water. The temperature was maintained at 25°C.

4.2 Results for the culture of the aniline acclimated sludge with r.p.-TDI (Culture I)

In this chapter, the quantity of r.p.- TDI was expressed by dividing the total amount of COD of added TDI into water by the whole volume of sludge solution.

4.2.1 pH

Fig. 4-1 shows pH change of the sludge which had been acclimated with aniline for the addition of r.p.-TDI and also aniline.
In the initial period it increased and then steady value of about 7.6 was obtained.

4.2.2 MLSS

The large fractuation of MLSS was observed in Fig. 4-2. As a whole, MLSS decreased gradually. The change depended on the addition of aniline. As seen in this figure the addition of aniline increased MLSS. r.p.-TDI alone could not raise MLSS.

4.2.3 SVI

Fig. 4-3 gives the change of sludge volume index. It decreased from 40 mℓ/g to 20.

4.2.4 COD of top water

COD of top water before the addition of aniline and r.p.-TDI was given in Fig. 4-4. This value roughly corresponded to the concentration of r.p.-TDI. (It was lover in the initial period).

4.2.5 Respiration Rates

Fig. 4-5 shows the respiration rate before the addition of r.p.-TDI and aniline.
In the initial period, the detectable respiration

rate was observed. However, after 30 days it went down to the undetectable level. The respiration rate after the addition of r.p.-TDI and aniline was shown in the lower part of Fig. 4-5. For the initial 20 days, relatively high value was obtained. However, in the later period, it became very low. On the 55th day, it shows considerably high value. It should be noted that r.p.-TDI had not been added for a few days before this peak appeared.

4.2.6 Biological Phase

No protozoans was observed in the course of the present experiment.

4.3 Discussions for the culture of the aniline acclimated sludge with r.p.-TDI (Culture I)

The change of pH in the initial 20 days would be due to the addition of aniline because the metabolic activity of aniline reduced pH In this period, MLSS was maintained at high value and COD of top water was low. Taking into account the low concentration of r.p.-TDI, the sludge was active with respect to aniline and the effect of r.p.-TDI was slight. This was also supported by the high respiration activity in this period. After this period, the total activity of sludge was gradually reduced.
However, the activity of the sludge could be recovered during 55 days. After about 100 days' culture, activity could not return any more.
In the experiment of 130 days, r.p.-TDI could not be metabolized and hindered the activity of the sludge.

4.4 Results for the culture of the CSL acclimated sludge with r.p.-TDI (Culture II)

4.4.1 pH

Fig. 4-6 gives the change of pH during the culture of CSL acclimated sludge with r.p.-TDI and also CSL. The value was maintained around 7.6. The absence of CSL generally increased pH.

4.4.2 MLSS

The change of MLSS during culture was shown in Fig. 4-7.

In the initial period where CSL was not given (0+0 30th day), MLSS decreased. The addition of CSL multiplicated MLSS. After 70th day it remained around 2200 ppm though CSL was not fed.

4.4.3 SVI

SVI was kept in the range of 30 to 40 as shown in Fig. 4-8.

4.4.4. COD

COD of top water is given in Fig 4-9.

In the initial period, it increased with the addition of r.p.-TDI. The increased concentration of CSL provisionally lowered it for a while. For the longer culture, COD stayed around 25 ppm in the absence of CSL.

4.4.5 Respiration rates

Fig. 4-10 gives the respiration rates of the sludge before and after the addition of r.p.-TDI and also CSL, respectively. Both respiration rates responded sensitively to the addition of CSL. They were almost zero in the initial period as long as CSL was not added.

The addition of CSL drastically enhanced both respiration rates.

However, in the latter period (after 60th day) they fell off to zero and did not respond to the addition of CSL. This indicated that r.p.-TDI destroyed the respiratory activity.

4.5 Discussion for the culture of the CSL acclimated sludge with r.p.-TDI (Culture II).

Generally, the behaviours of culture II resembled those of culture I. As far as the change of MLSS concerned, r.p.-TDI seemed to be metabolized because MLSS maintained a roughly constant value in the long culture where CSL was not given. However, the hgih values of COD in the latter period were contradictory with this possibility. The results for the respiration rates could support the hindrance effect of r.p.-TDI for activated sludge.

In conclusion, r.p.-TDI was not metabolized by the activated sludge and hindered its activity.

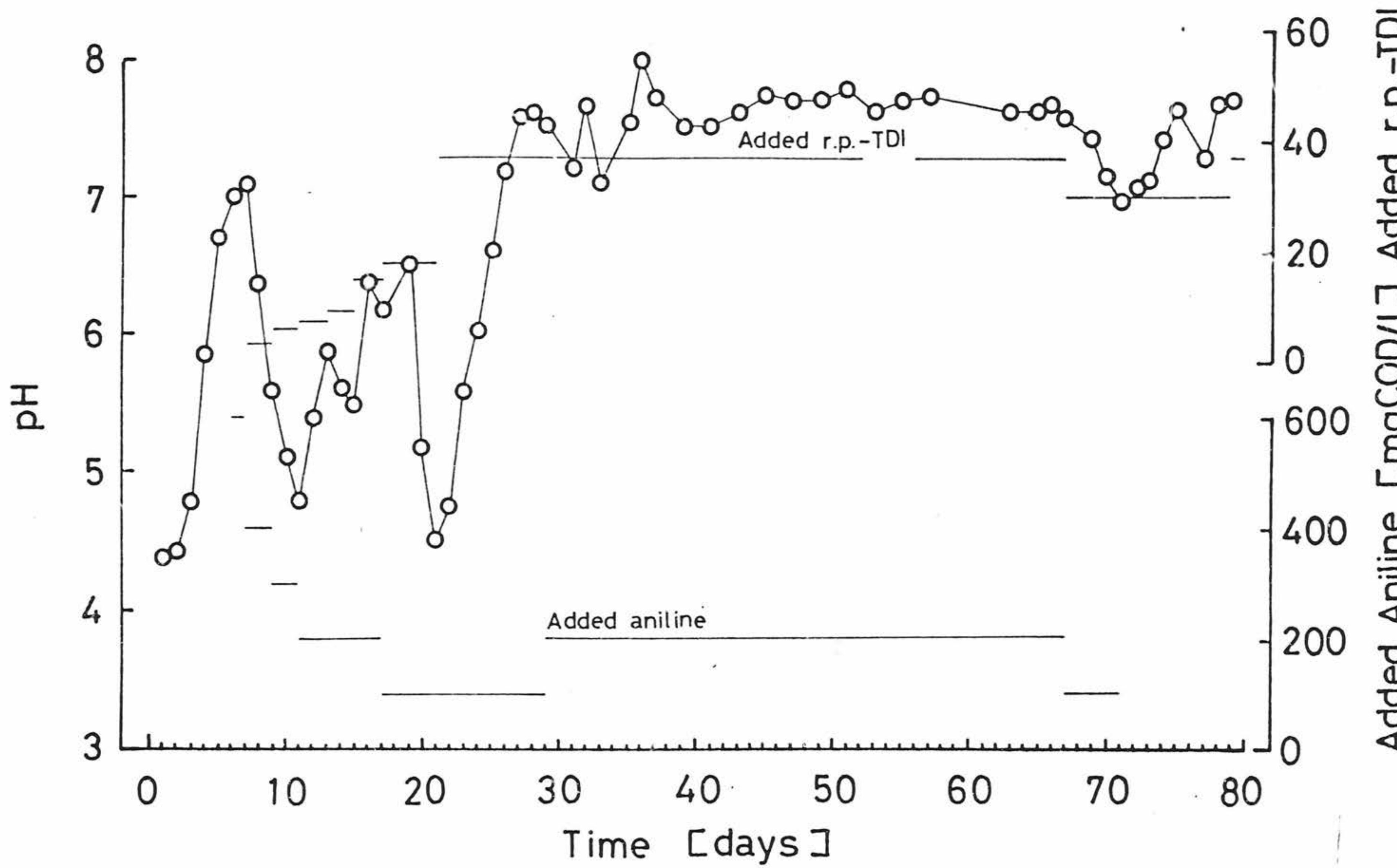


Fig. 4-1 pH change for culture (I) (1)

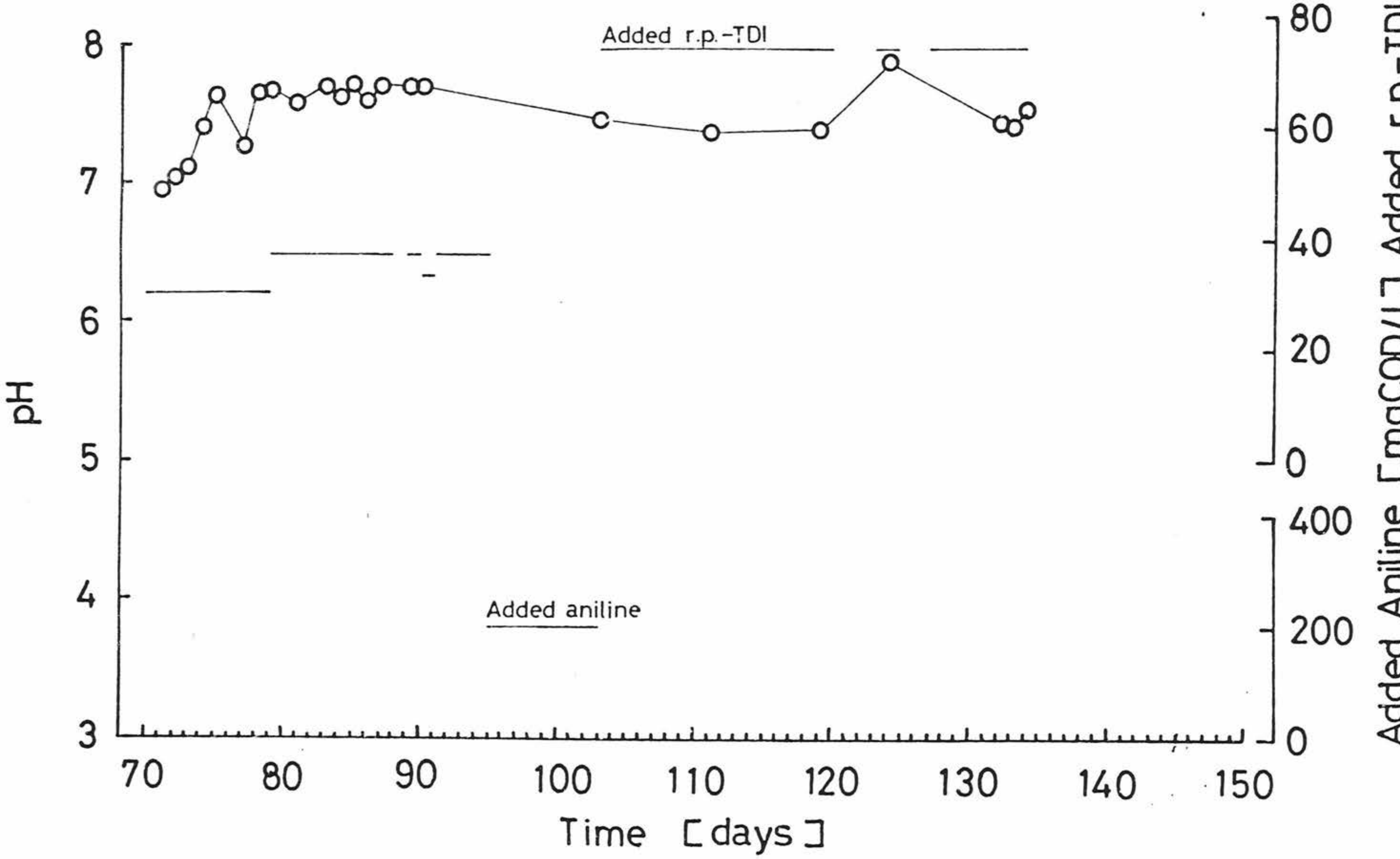


Fig. 4-1 pH change for culture (I) (2)

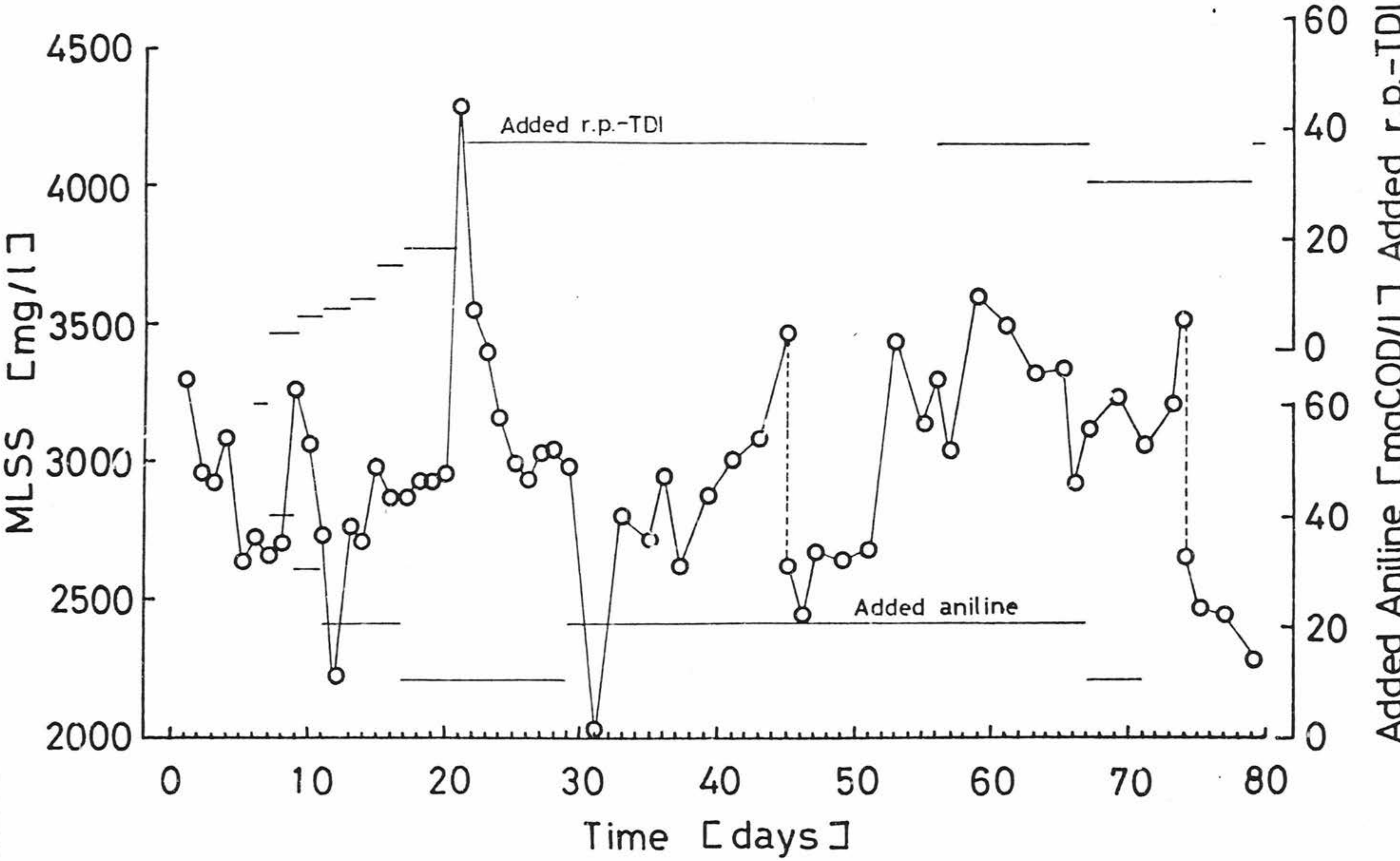


Fig. 4-2 MLSS for culture (I) (1)

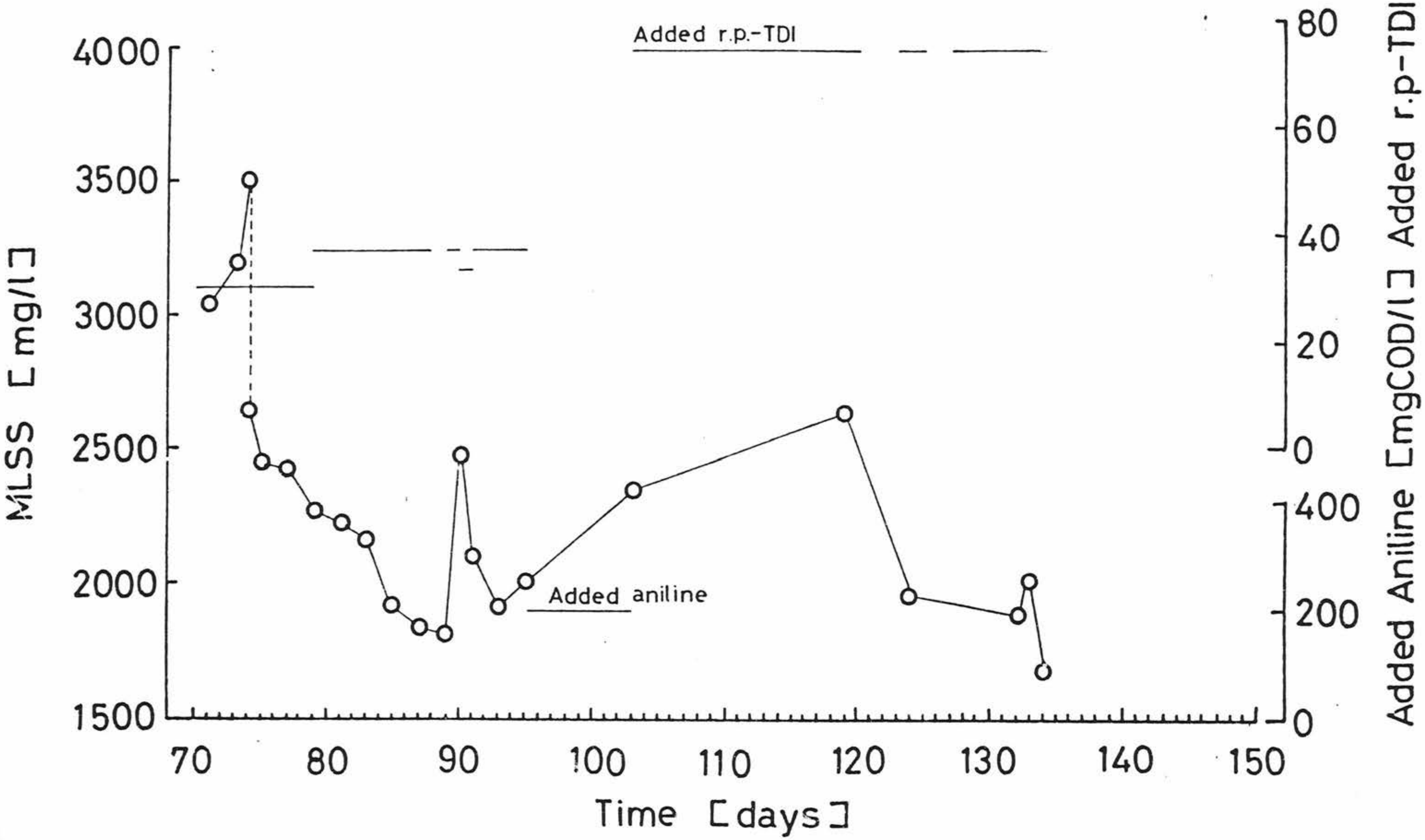


Fig. 4-2 MLSS for culture (I) (2)

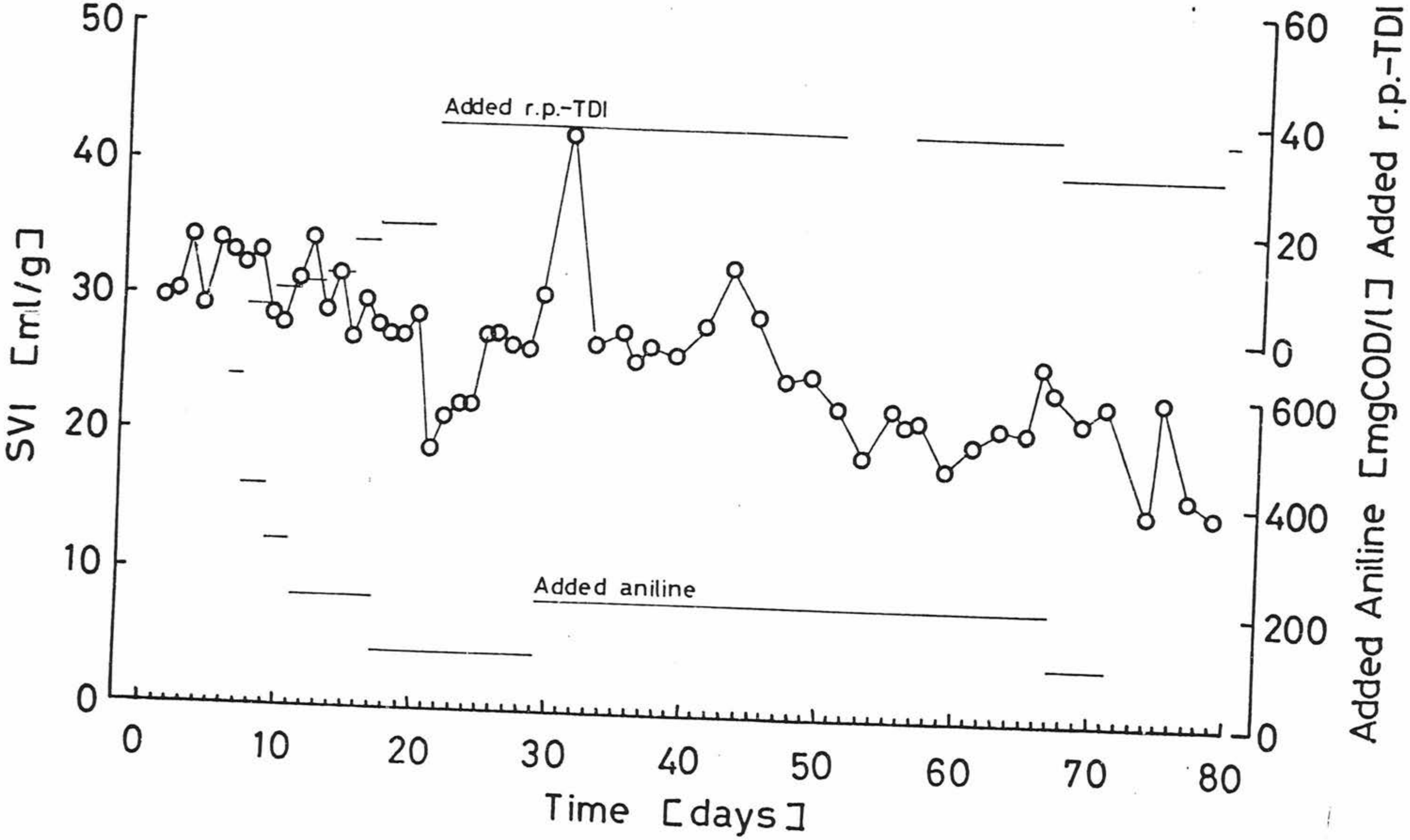


Fig. 4-3 SVI for culture (I) (1)

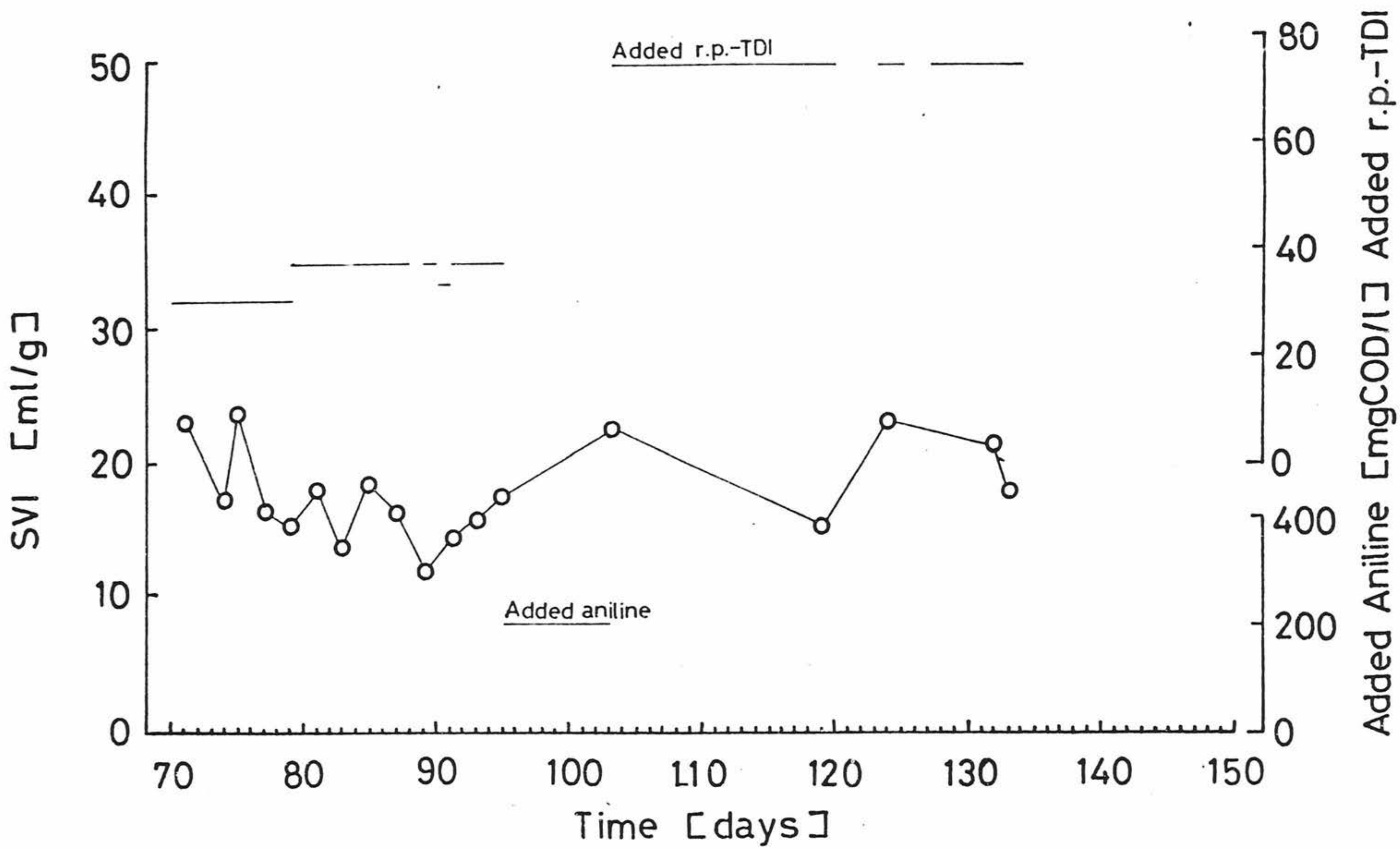


Fig. 4-3 SVI for culture (I) (2)

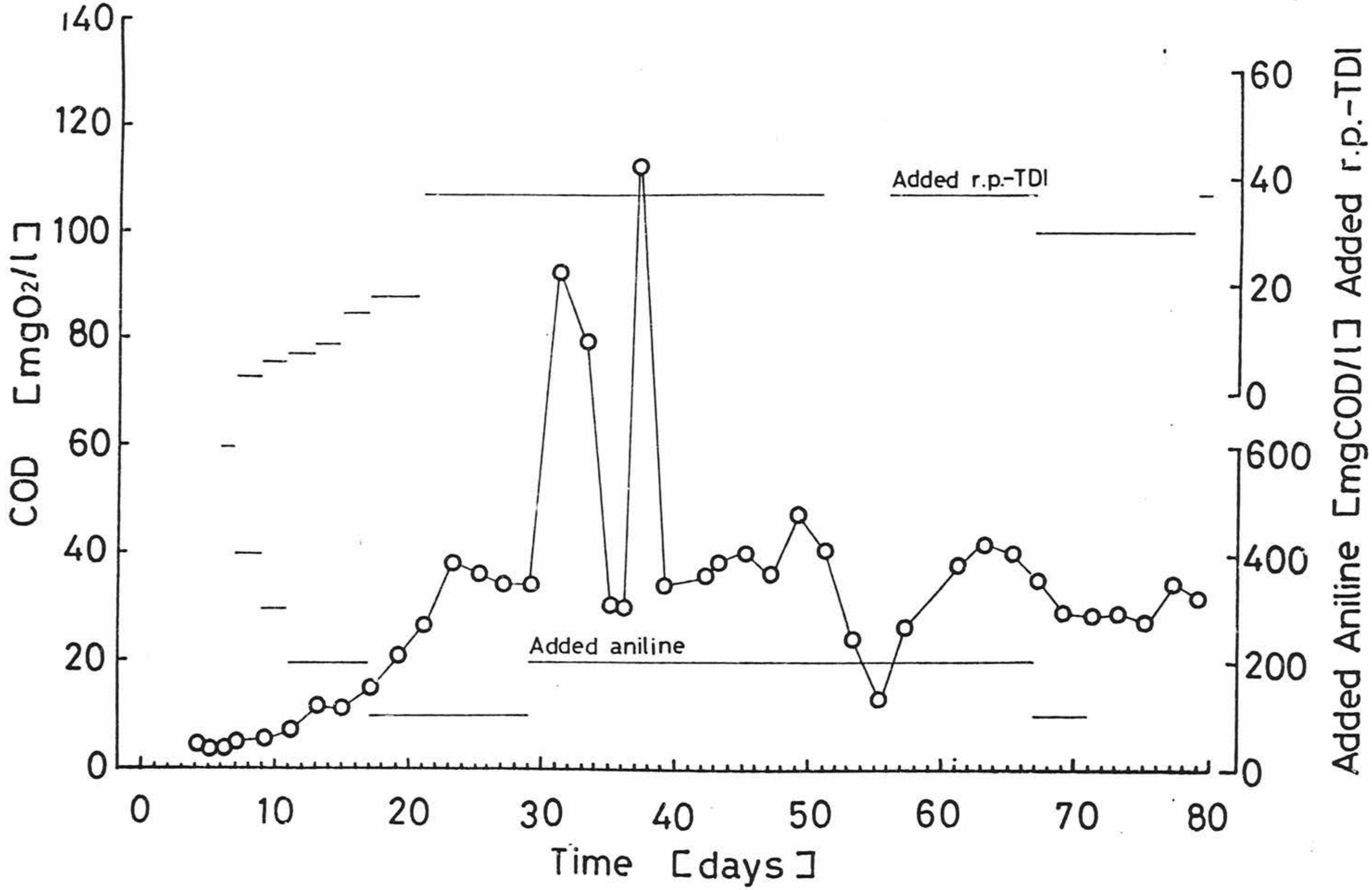


Fig. 4-4 COD of top water for culture (I) (1)

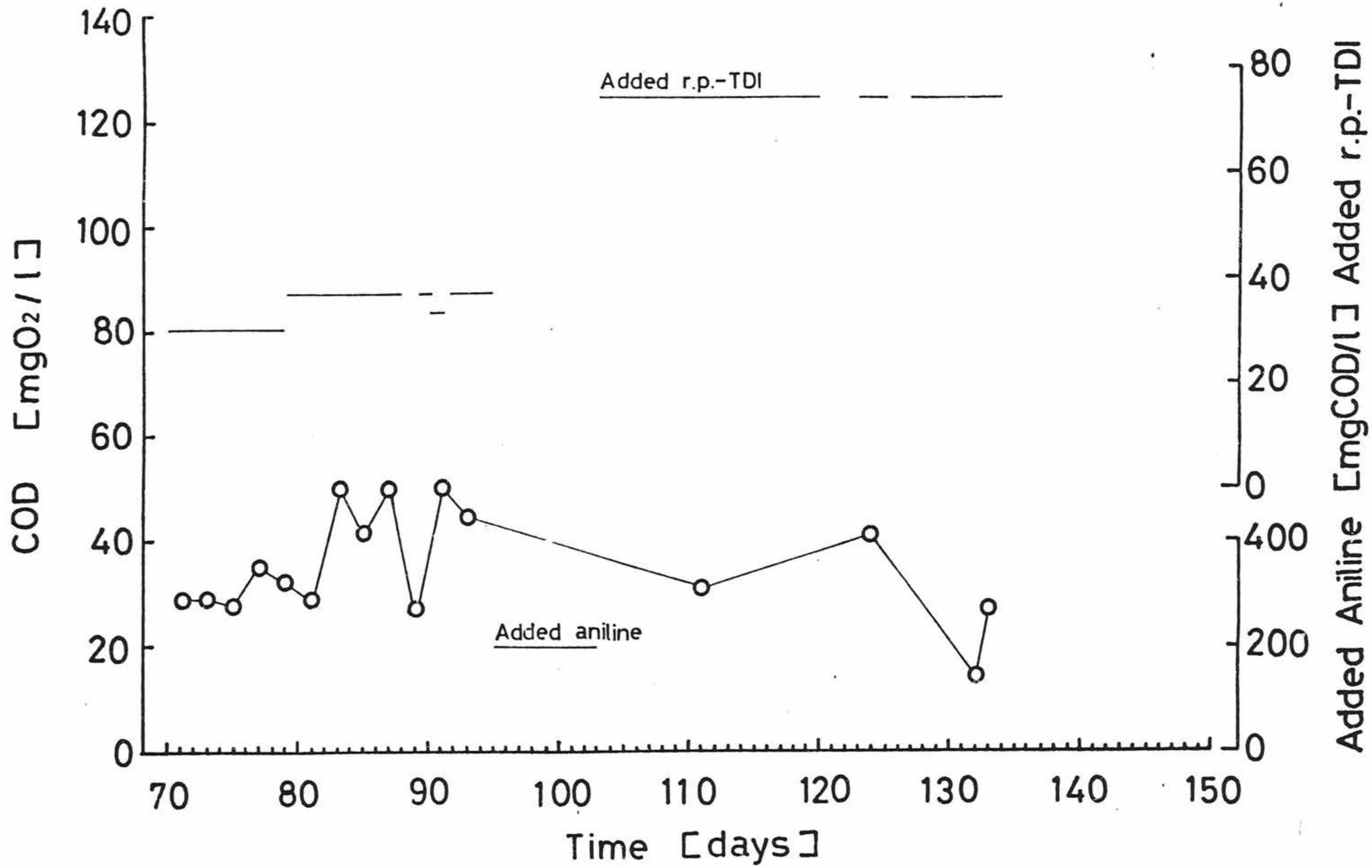


Fig. 4-4 COD of top water for culture (I) (2)

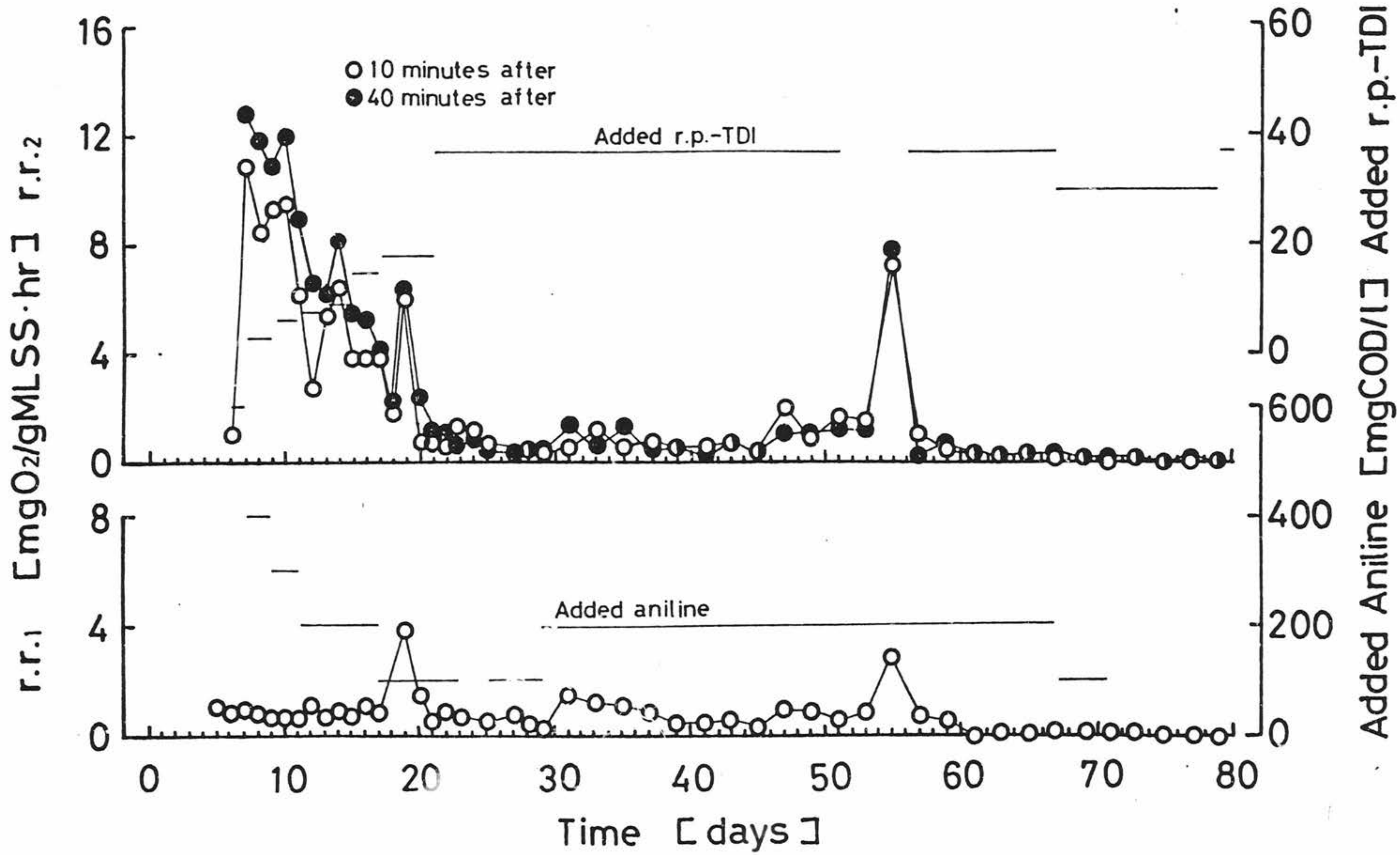


Fig. 4-5 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I) (1)

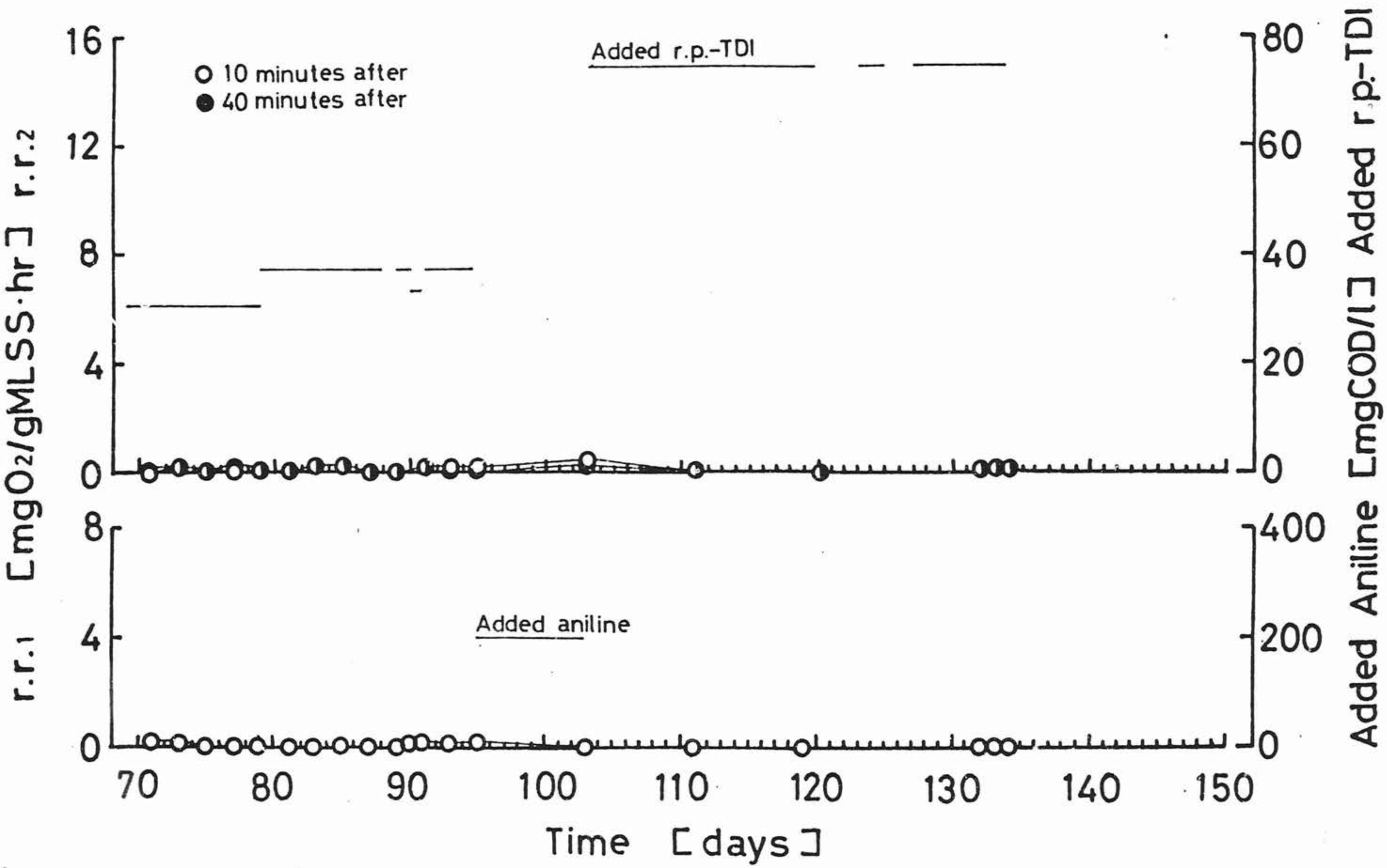


Fig. 4-5 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I) (2)

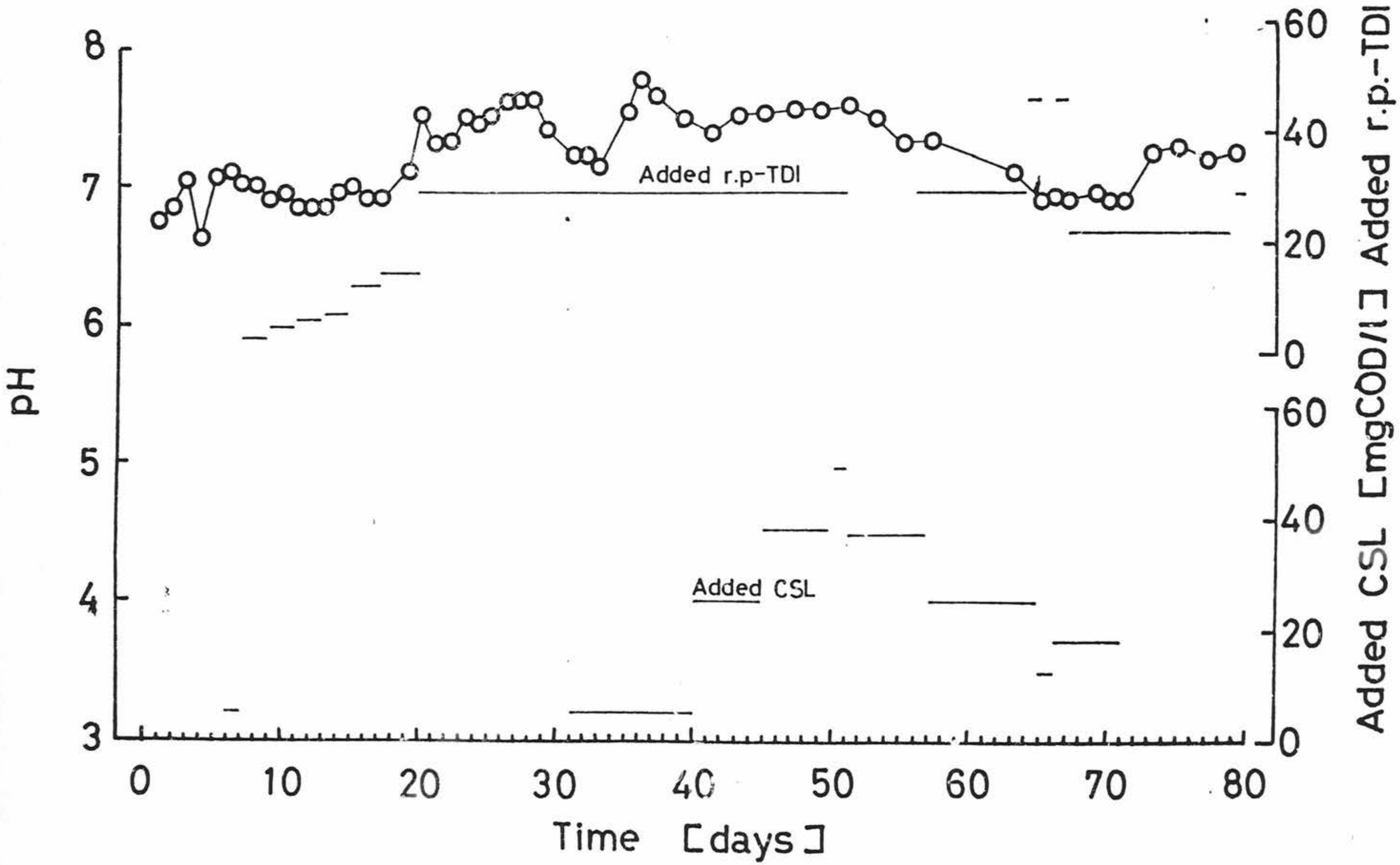


Fig. 4-6 pH change for culture (II) (1)

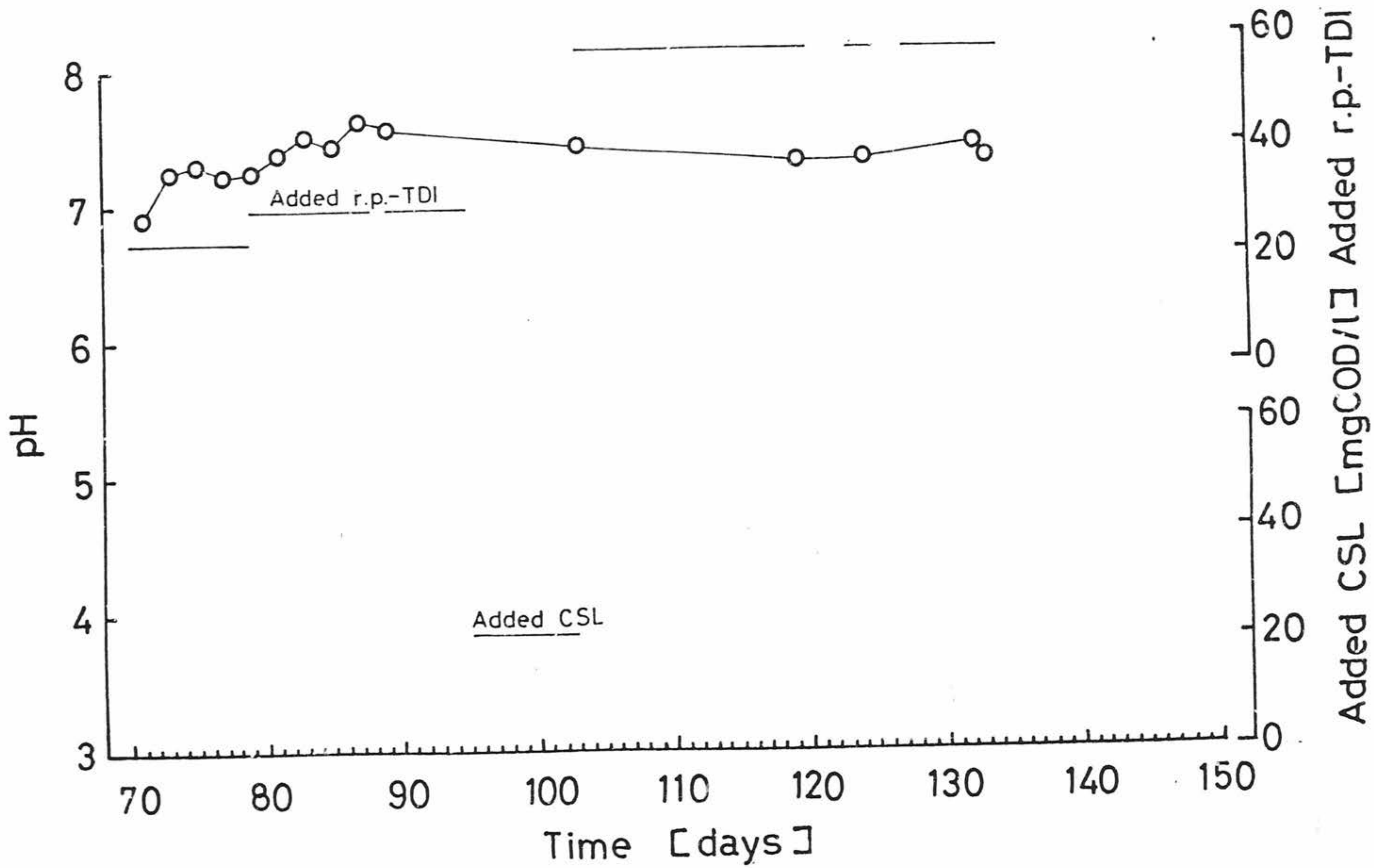


Fig. 4-6 pH change for culture (II) (2)

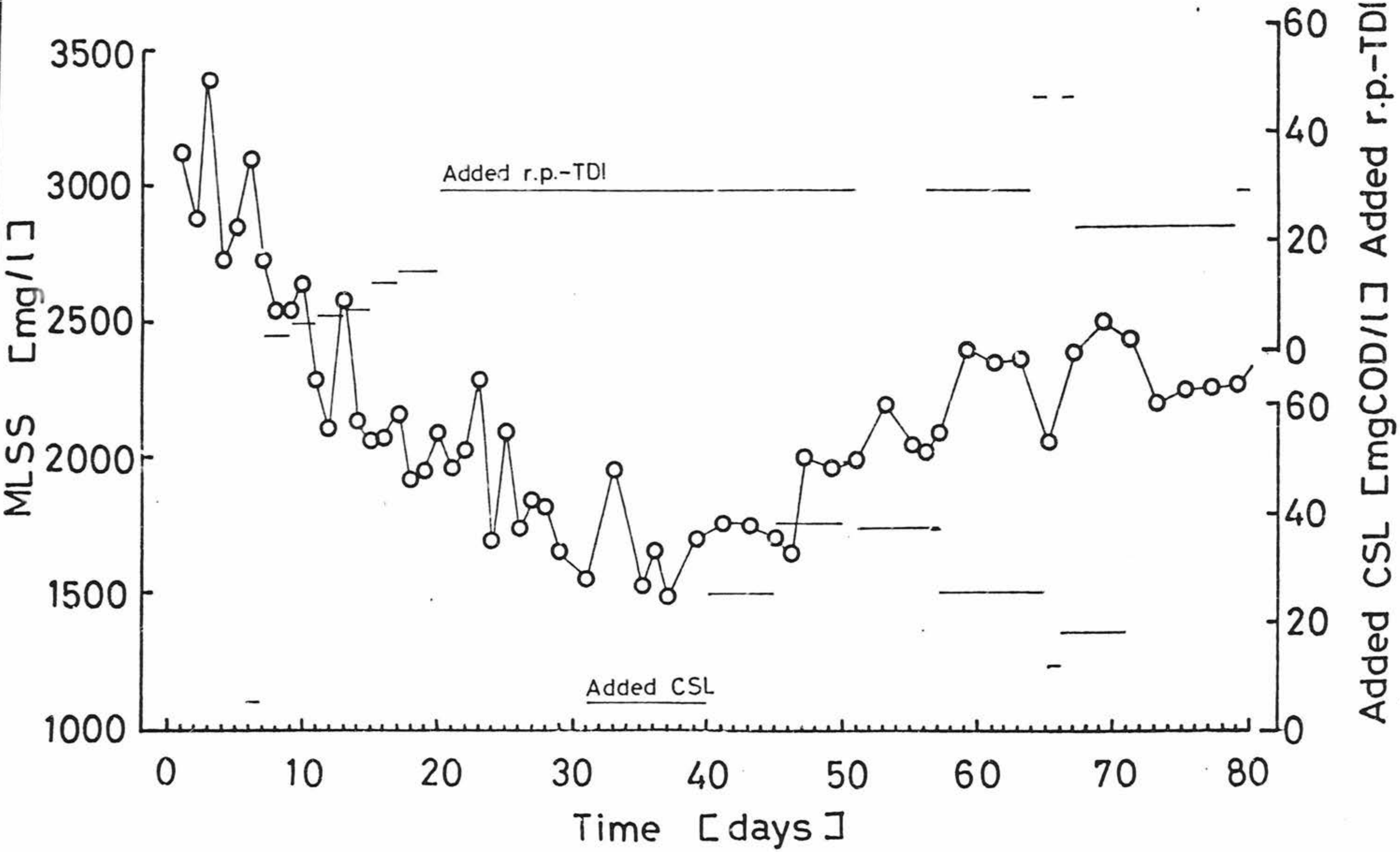


Fig. 4-7 MLSS for culture (II) (1)

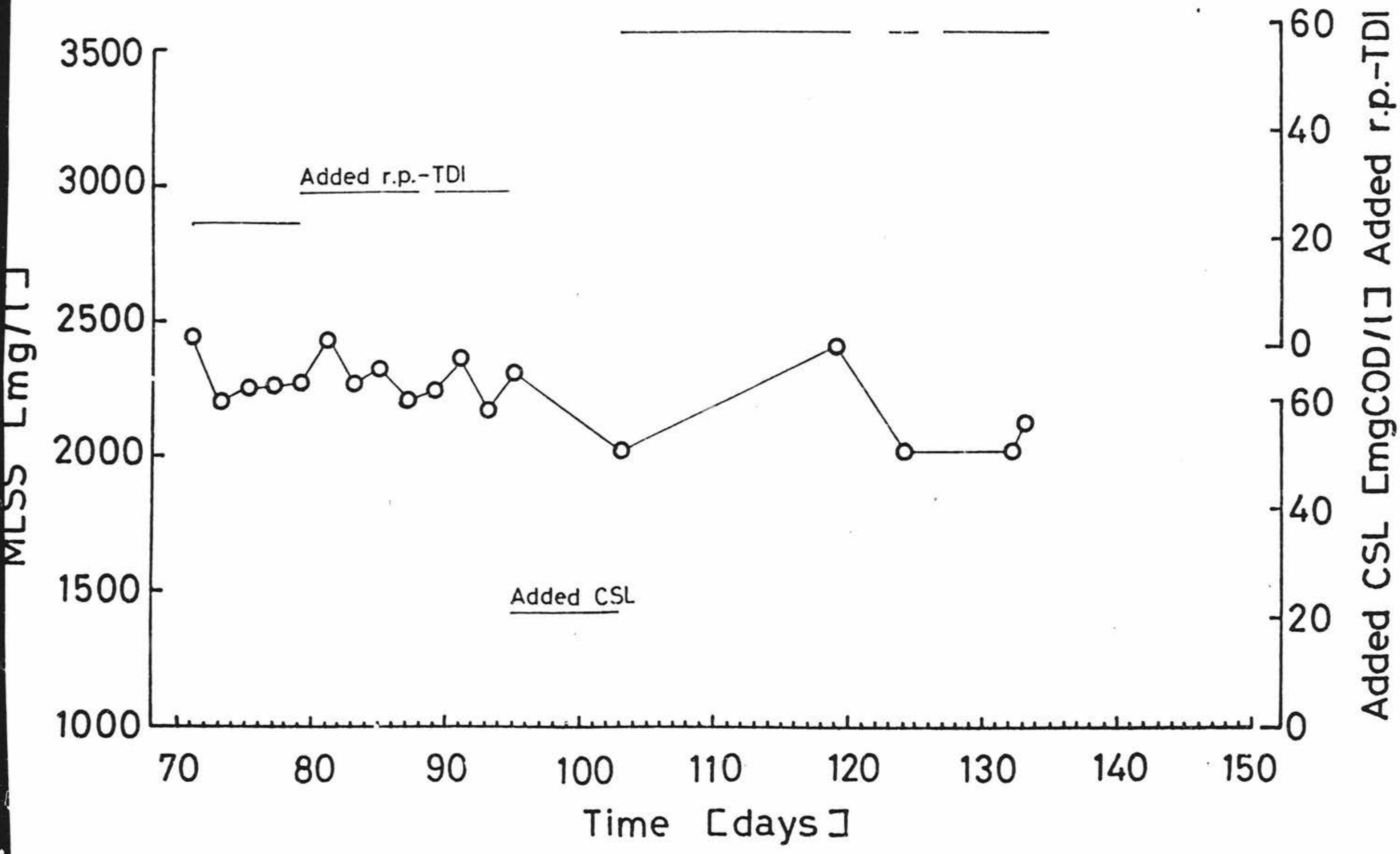


Fig. 4-7 MLSS for culture (II) (2)

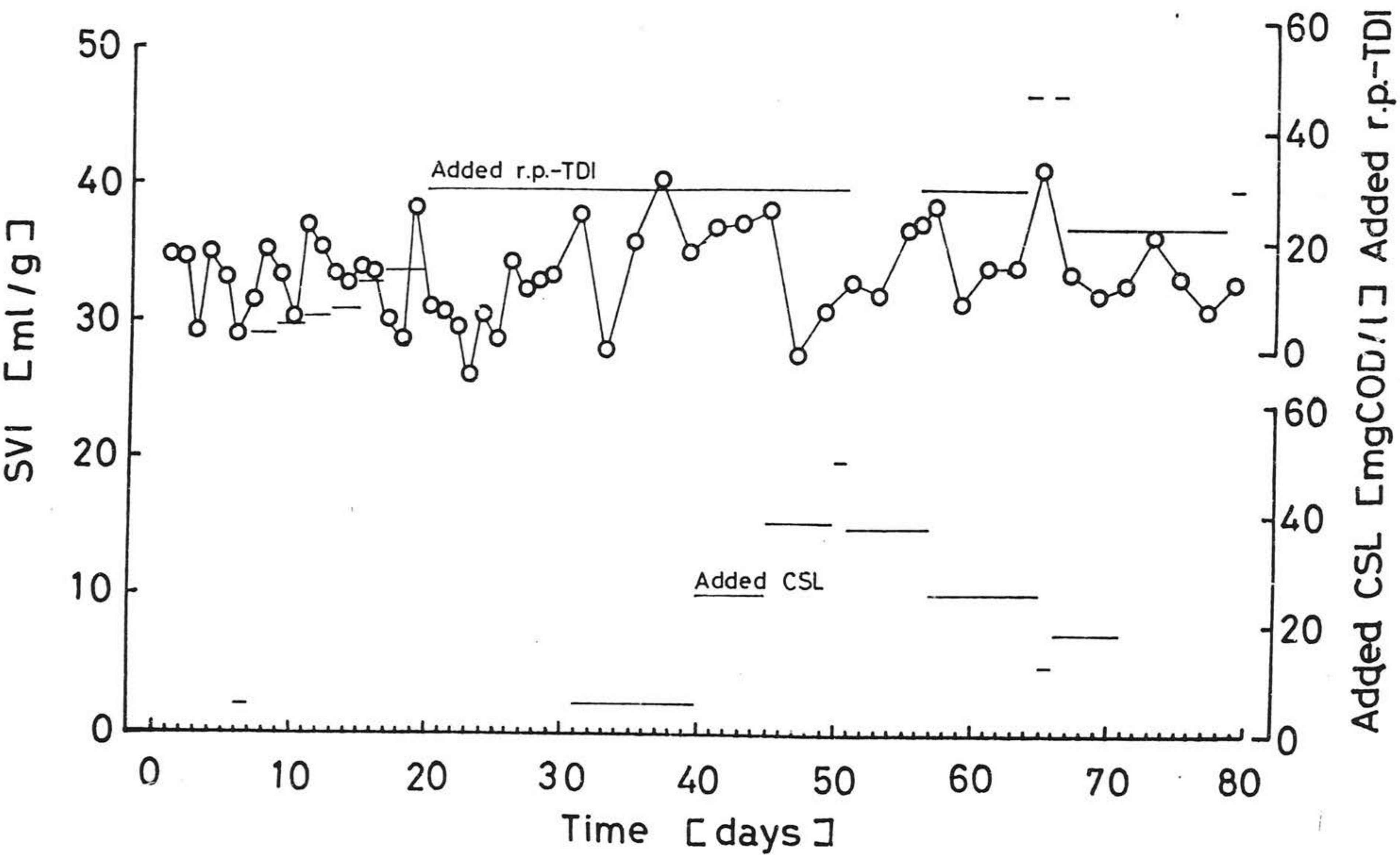


Fig. 4-8 SVI for culture (II) (1)

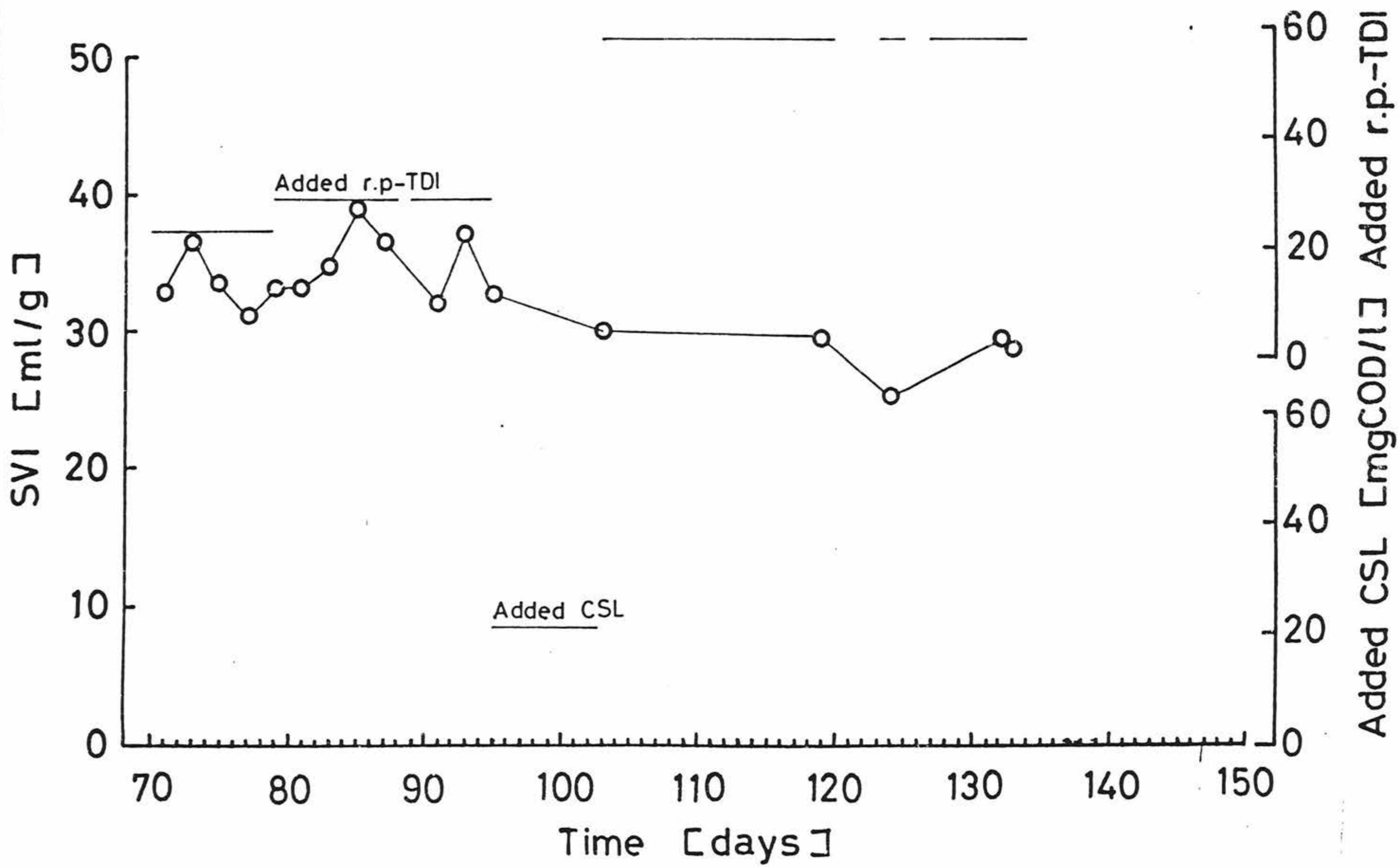


Fig. 4-8 SVI for culture (II) (2)

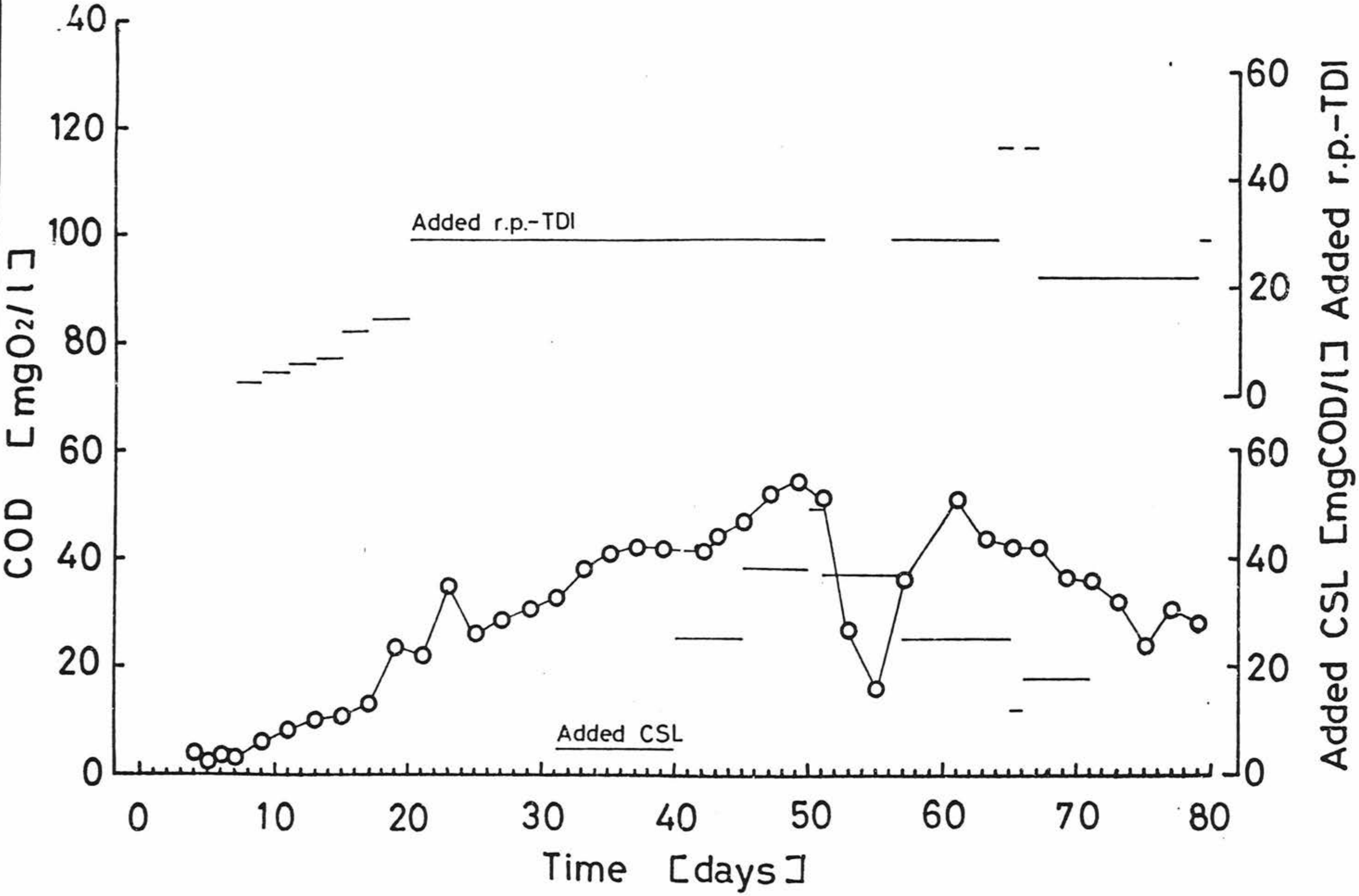


Fig. 4-9 COD of top water for culture (II) (1)

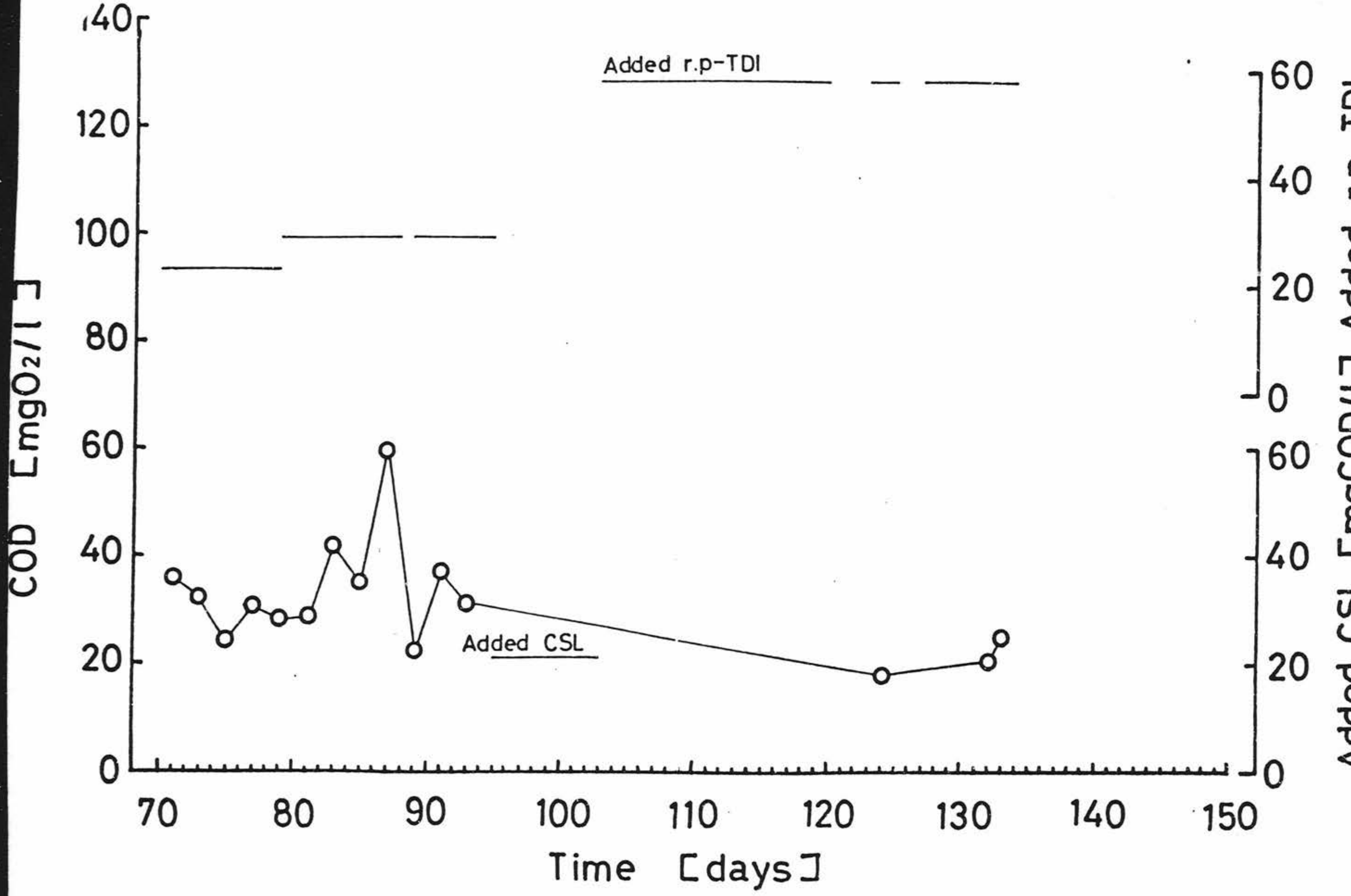


Fig. 4-9 COD of tcp water for culture (II) (2)

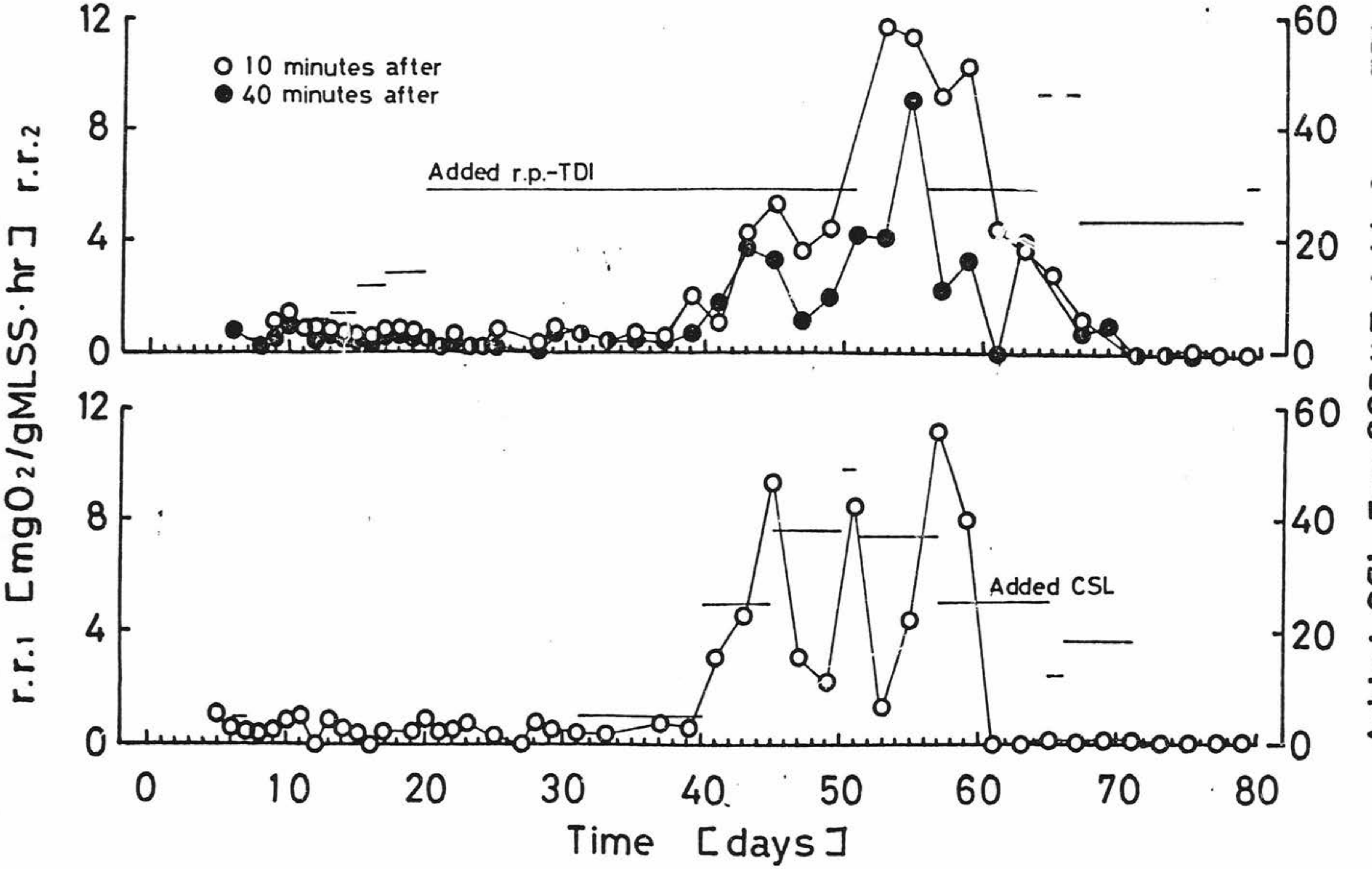


Fig. 4-10 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II) (1)

5. Culture of activated sludge with tolylene diamine

5.1 Introduction

As has been described in the previous report (III Project No. FE-E-15) tolvlendiisocyanate reacts with water to give tolylene diamine.

$$R(NCO)_2 + 2H_2O \longrightarrow R(NH_2)_2 + 2CO_2$$

Thus, tolylene diamine(TDA) could be a pollutant in the effluent from water scrubber of the air including tolylendiisocyanate gas.

The effect of this effluent on the activated sludge should be considered from the environmental point of view.

As has already been reviewed in Chapter 2, the compounds whose structure were similar to aniline could be metabolized in the aniline-acclimated sludge.

In this experiment, 2,6-tolylene diamine (2,6-TDA) whose solubility was relatively higher than other isomers was examined.

5.2 Experimental

The experimental procedures were almost similar to those of Chapter 4.

The activated sludge which was acclimated with aniline or CSL was bring into the culture vessel of about 30ℓ. The sludges were multiplicated upto the desired density.

Then, the feeding of nutritions was stopped under the aeration until endgeneous conditions were attained.

The top water of 18ℓ was replaced every day with the buffer solution whose composition was given in Chapter

3. At the same time, the assigned quantity of nutritions was added. The temperature was maintained about 25°C.

5.3 Results for the culture of the aniline acclimated sludge with 2, 6 TDA (Culture I)

In this chapter the quantity of TDA and aniline was expressed in terms of COD equivalents being similar to that in the previous chapters.

5.3.1 pH

In the initial period (0 to 15th day), where the concentration of added aniline was high and that of TDA was low, pH decreased monotonically to about 4. (Fig. 5-1). From 16th day pH started to increase.

The anomaly high value of pH appearing on 21st day was due to the neutralization with alkaline solution.

After 40th day, pH roughly traced the concentration of added TDA, i.e. the increase in the concentration of added TDA brought about the higher value of pH.

The critical concentration of TDA which induced the increase in pH, seemed to be about 15 mg COD/ℓ.

5.3.2 MLSS

Fig. 5-1 shows the value of MLSS during culture.

It was kept almost constant before 70th day regardless of the concentrations of added TDA and aniline.

Thereafter, MLSS gradually decreased as a whole.

5.3.3 SVI

As shown in Fig. 5-3, SVI was kept between 30 and

40 mℓ/g during the culture.

5.3.4 COD

Fig. 5-4 gives COD of top water immediately before its replacement.

It was kept less than 15 mg O_2/ℓ as long as the concentration of added TDA was low.

However, the addition of TDA higher than 18 mg COD/ℓ brought about the remarkable increase of COD.

5.3.5 Respiration rates

Respiration rates immediately before the addition of nutritions and at 30 minutes after their addition are given in Fig. 5-5.

The respiration rate immediately before the addition stayed at very low value.

This indicated that the sludge was in endgeneous conditions before the addition of nutritions or it was inactive.

The respiration rate at 30 minutes after the addition of nutritions was maintained at high value up to 55th day. After then it was kept as low as that immediately before the addition.

It was clearly shown that the loading of TDA as much as 20 mg COD/ℓ destroyed the respiration activity of the sludge which could not have been recovered any more.

5.3.6 Treatment efficiency

Treatment efficiency was calculated from COD's of added nutritions and top water as given in Fig. 5-6.

It was almost kept above 90% during the culture. As the amount of added aniline was much larger than TDA, aniline was well metabolized throughout the culture.

5.3.7 Biological phase

In the initial half of the culture vorticella and rotifera were found.

Rotifera was a only observable protozoans in the latter half and its activity was low.

The color of the sludge changed from gray to black gradually.

The high loading of TDA changed the color from black to dark red immediately.

5.4 Discussions for culture of the aniline acclimated sludge with 2, 6 TDA (Culture I).

The review of results offered the general information that pH, COD, and respiration rates responded sensitively to the addition of TDA but MLSS and SVI were not affected.

In the initial period (0 to 6th day) aniline was fed singly.

The decrease in pH in this period was owing to nitrifying reaction.

The elevation of pH in accordance with the addition of TDA would result from the inhibition of nitrifying reaction by TDA.

Consistently, COD of effluent increased with the addition TDA.

The drastic increase in pH and COD and decrease in respiration rates appeared when TDA of 24.4 ppm was given.

This indicated that the durability limit of TDA to the sludge seemed to exsist.

The critical value could be 15 to 20 mg COD/ℓ of TDA from the comparison of data.

Once the sludge experienced TDA above this critical value, its activity was lost and hardly recovered.

The conclusion was that ;

(1) The addition of small amount of TDA to the aniline acclimated sludge slightly reduced the activity.

(2) The critical concentration of TDA which killed the activity of the sludge was found.

Its value was between 15 and 20 mg COD/ℓ.

(3) As long as the concentration of TDA in the sludge was less than the critical value and the large amount of aniline was fed, TDA was not harmful to the sludge.

However, the decomposition and/or oxidation of TDA in this process were not always assured.

The difficulty in the analysis of TDA in the presence of excess amount of aniline remained the problem unsolved.

(4) It seemed difficult to culture the sludge with 2,,6 TDA exclusively of other nutritions.

5.5 Results for the culture of the CSL acclimated sludge with 2, 6 TDA (Culture II).

5.5.1 pH

In contrast to the case of aniline acclimated sludge, the change of pH did not sensitively respond to the concentration of added TDA but it became gradually higher with time as shown in Fig. 5-7.

5.5.2 MLSS

MLSS gradually decreased to about 2000 ppm as given in Fig. 5-8.

It could be recognized that the decrease in pH was detained by addition of CSL.

5.5.3 SVI

SVI gradually decreased from 80 to 40 as shown in Fig. 5-9.

This indicated that the sedimentation and coagulation were excellent.

5.5.4 COD

COD of the top water immediately before its replacement appears in Fig. 5-10. In the initial period COD stayed at about 5 ppm.

The addition of CSL and also TDA induced its gradual increase to about 10 ppm.

As the value itself was relatively low, the detailed discussion on its trend seemed to be in vain.

5.5.5 Respiration rates

Respiration rates immediately before and 30 minutes after the addition of CSL and also TDA are given Fig. 5-11. In the initial period where the concentration of added TDA was low, the addition of CSL rised the respiration rate 30 minutes after the addition (rr_2).

However, rr_2 decayed to almost nought as time passed.

The respiration rate immediately before the addition (rr_1) showed a slight increase in the middle of culture.

In the rest of the cultural interval rr_1 was undetectably low.

5.5.6 Visible observation

It was observed that the top water became turbid and the color of sludge changed to black.

5.6 Discussions for the culture of the CSL acclimated sludge with 2, 6 TDA (Culture II)

Being similar to the case of aniline acclimated sludge SVI maintained broadly constant value of 60 to 80, regardless of the concentration of added TDA.

However, the value itself was different from the case of aniline acclimated sludge where it was 30 to 40.

Though MLSS was not sensitively responsible to the change of added nutritions, it decreased gradually to 2000 ppm.

Thus, as far as MLSS concerned TDA seemed not always harmful.

However, the respiration rates and COD of top water suggested the degradation of activity of the sludge.

The respiration rate 30 minutes after the addition of nutritions (rr_2) exhibited the degradation of respiratory activity with time which would be closely related to the total activity of the sludge.

Here, it should be reminded that rr_2 decreased despite giving the same amounts of TDI and CSL constantly in the latter period.

In the same period COD showed the increasing trend. This indicated the degradation of treatability of the sludge.

The contradiction lying between the results of MLSS and of COD and respiration rates introduced the idea that TDA produced the sludge which was inactive not only to the metabolism of nutritions but also to the biological oxidation of itself.

It should be noteworthy that this inhibitive trend appeared at the concentration of TDA as low as 5 ppm.

This was compaired to the case of aniline acclimated sludge where the critical concentration of TDA was 15 to 20 ppm.

In conclusion, TDA even at low concentration inhibited gradually the metabolic activity of the sludge which cultured with CSL.

However, taking into account the previous experiment, the inhibitive action of TDA would be reduced by acclimating the sludge with aniline.

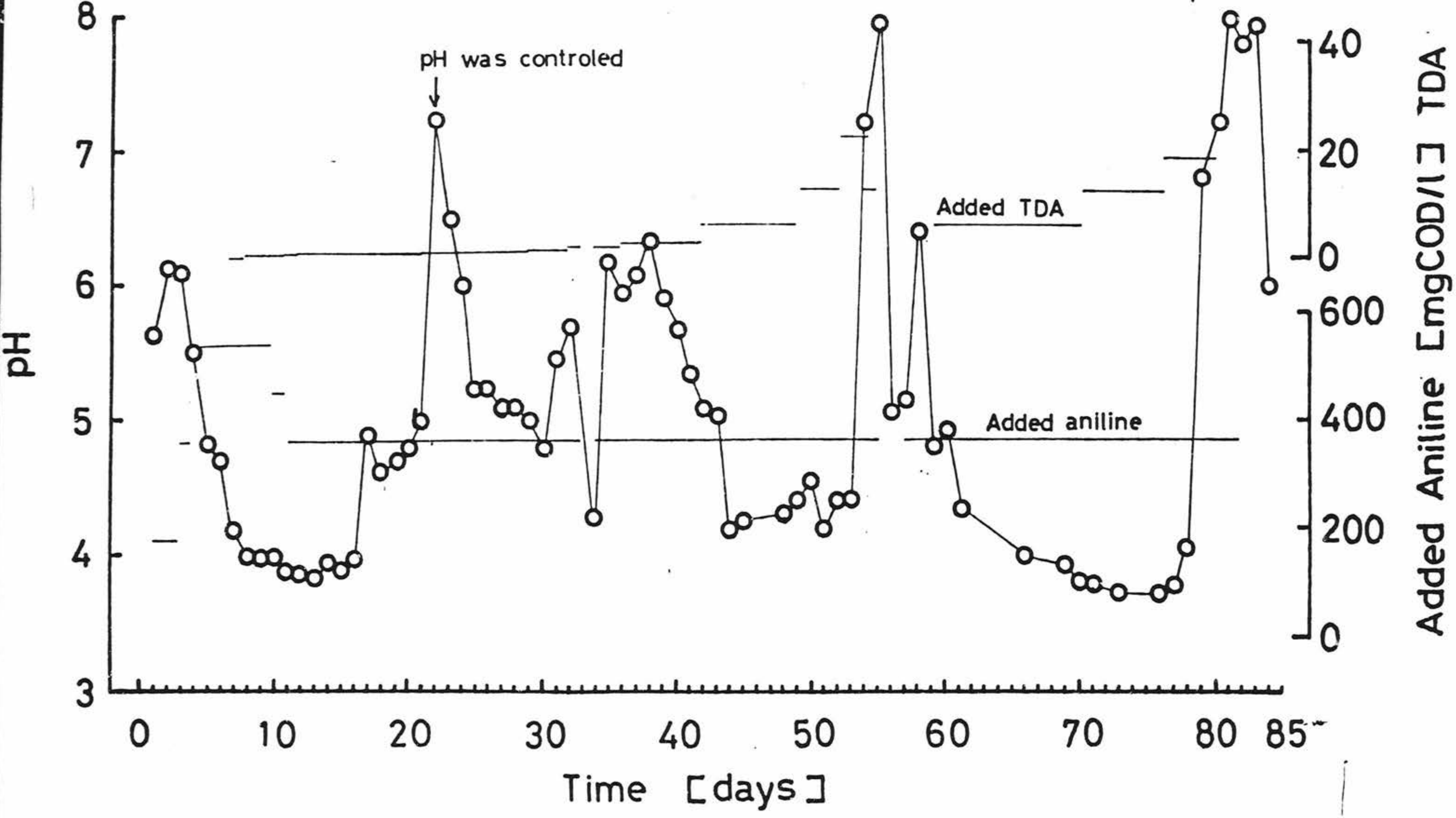


Fig. 5-1 PH change for culture (I)

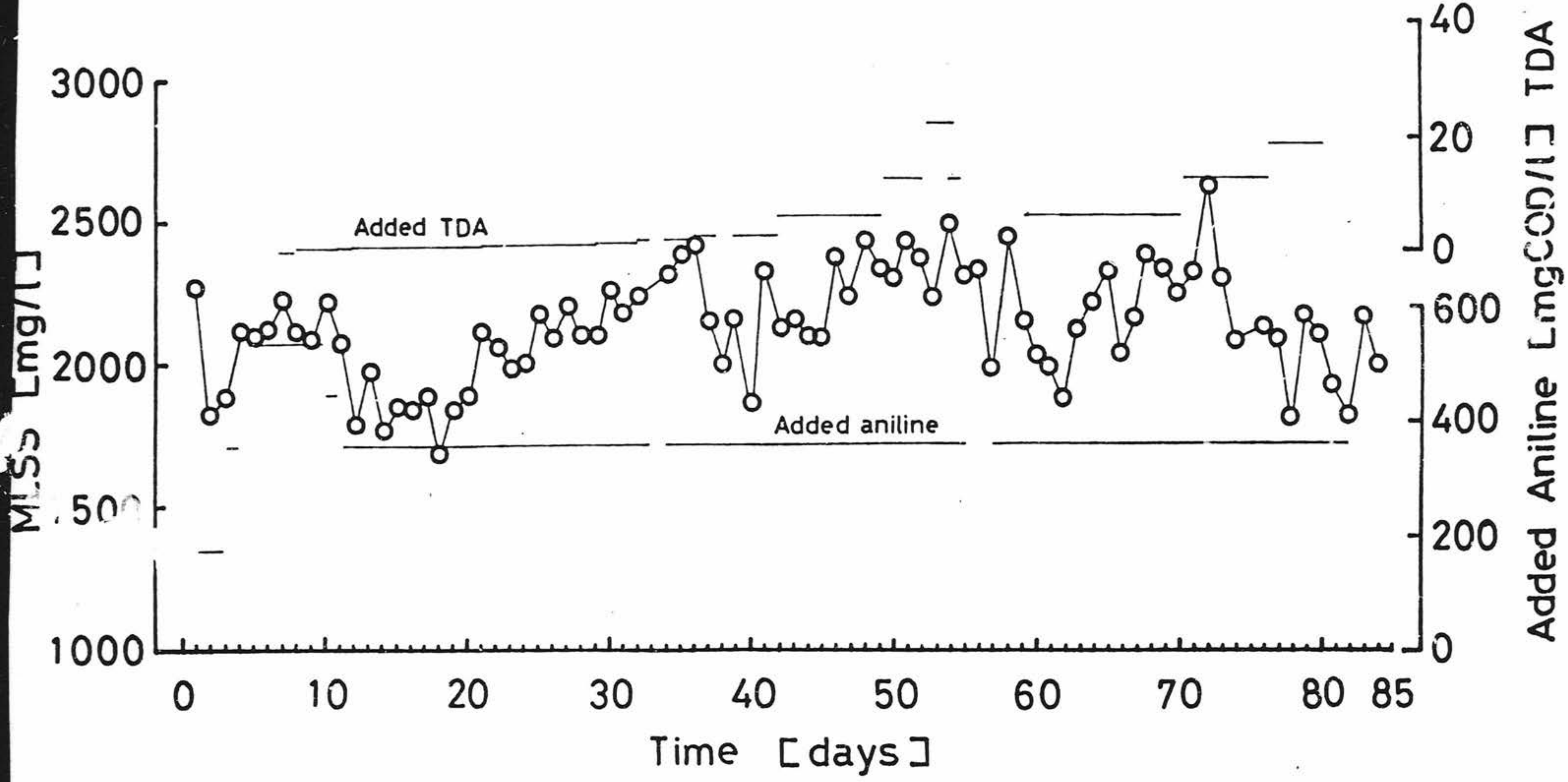


Fig. 5-2 MLSS for culture (I)

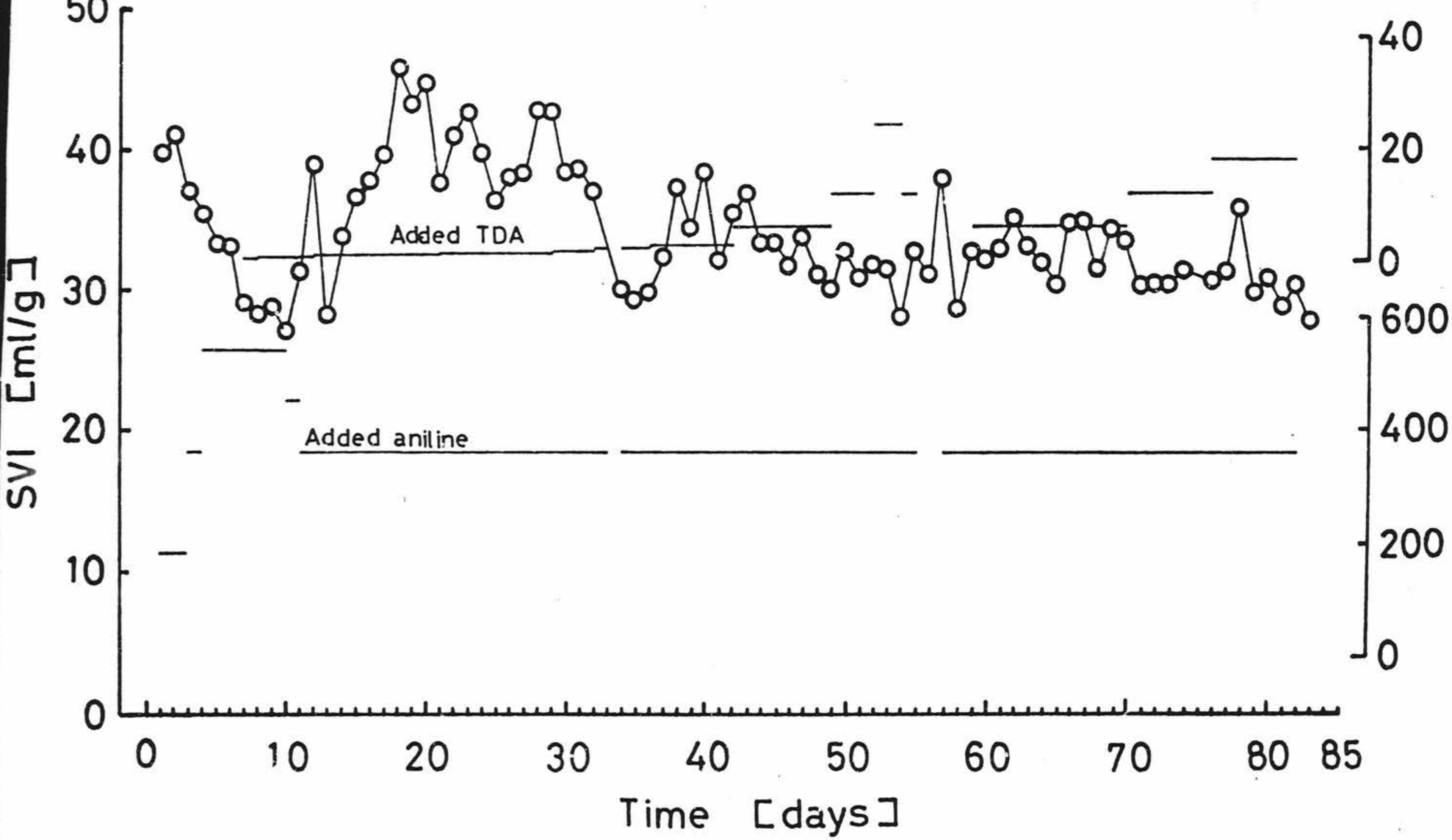


Fig. 5-3 SVI for culture (I)

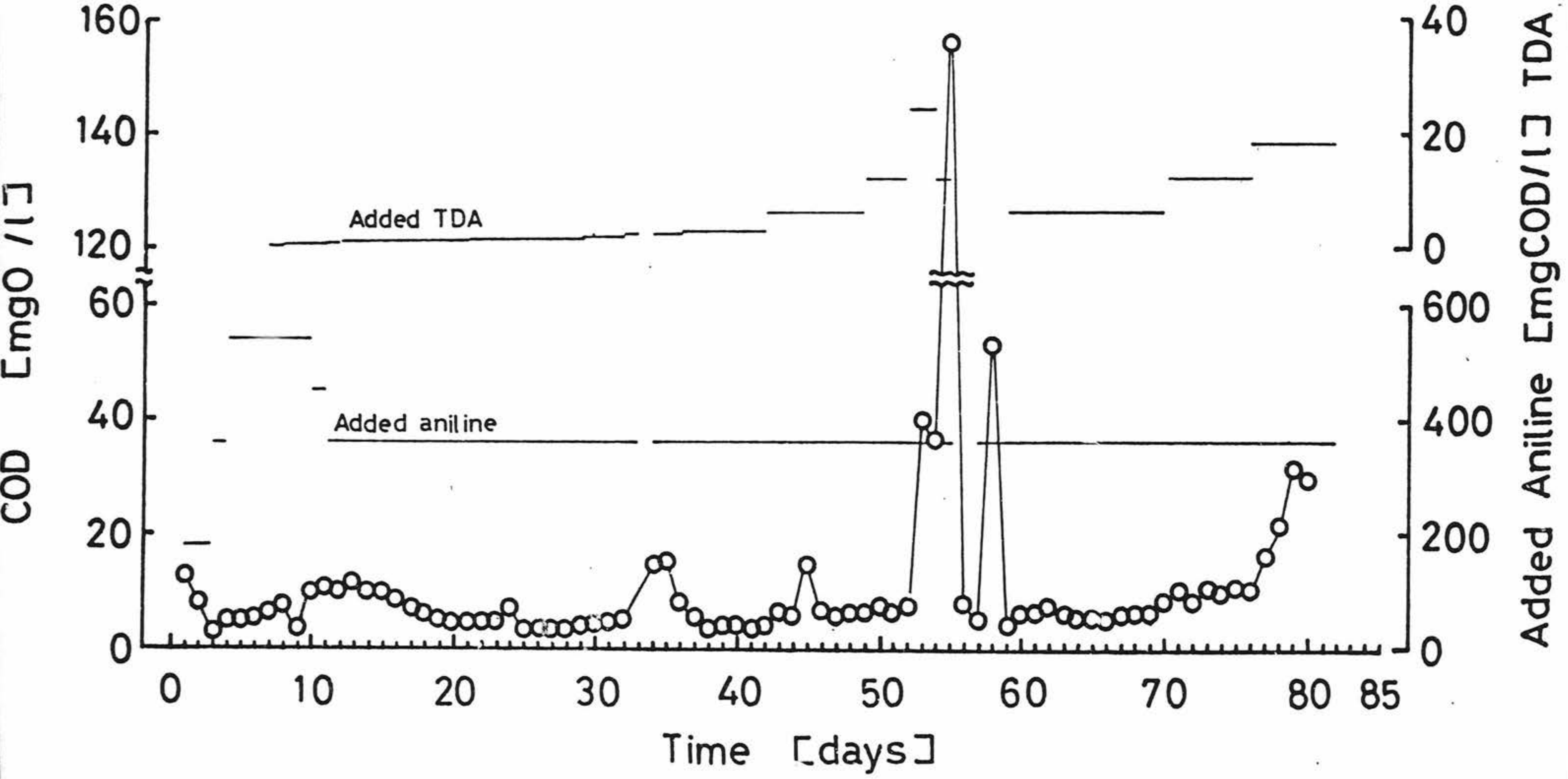


Fig. 5-4 COD of top water for culture (I)

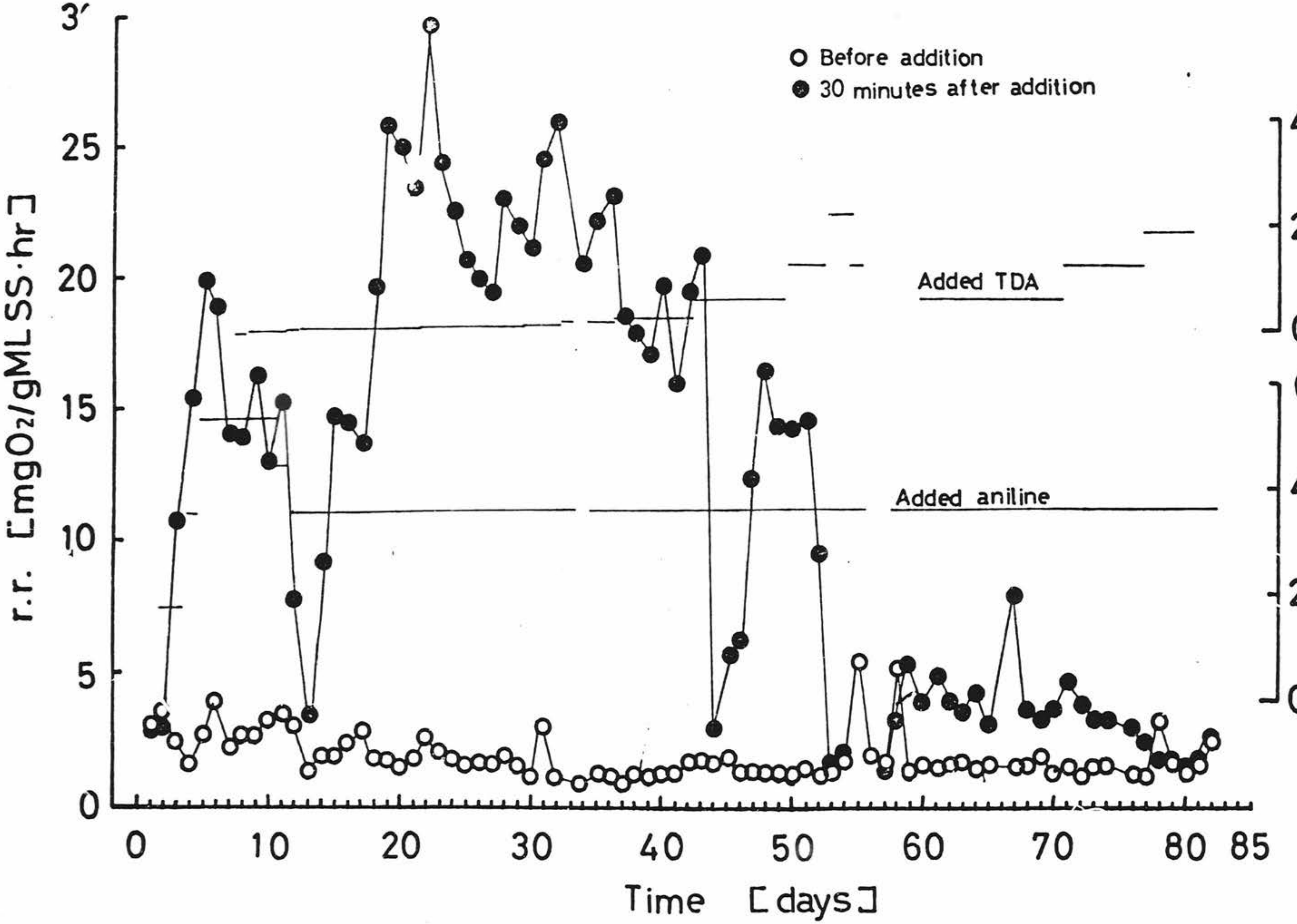


Fig. 5-5 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I)

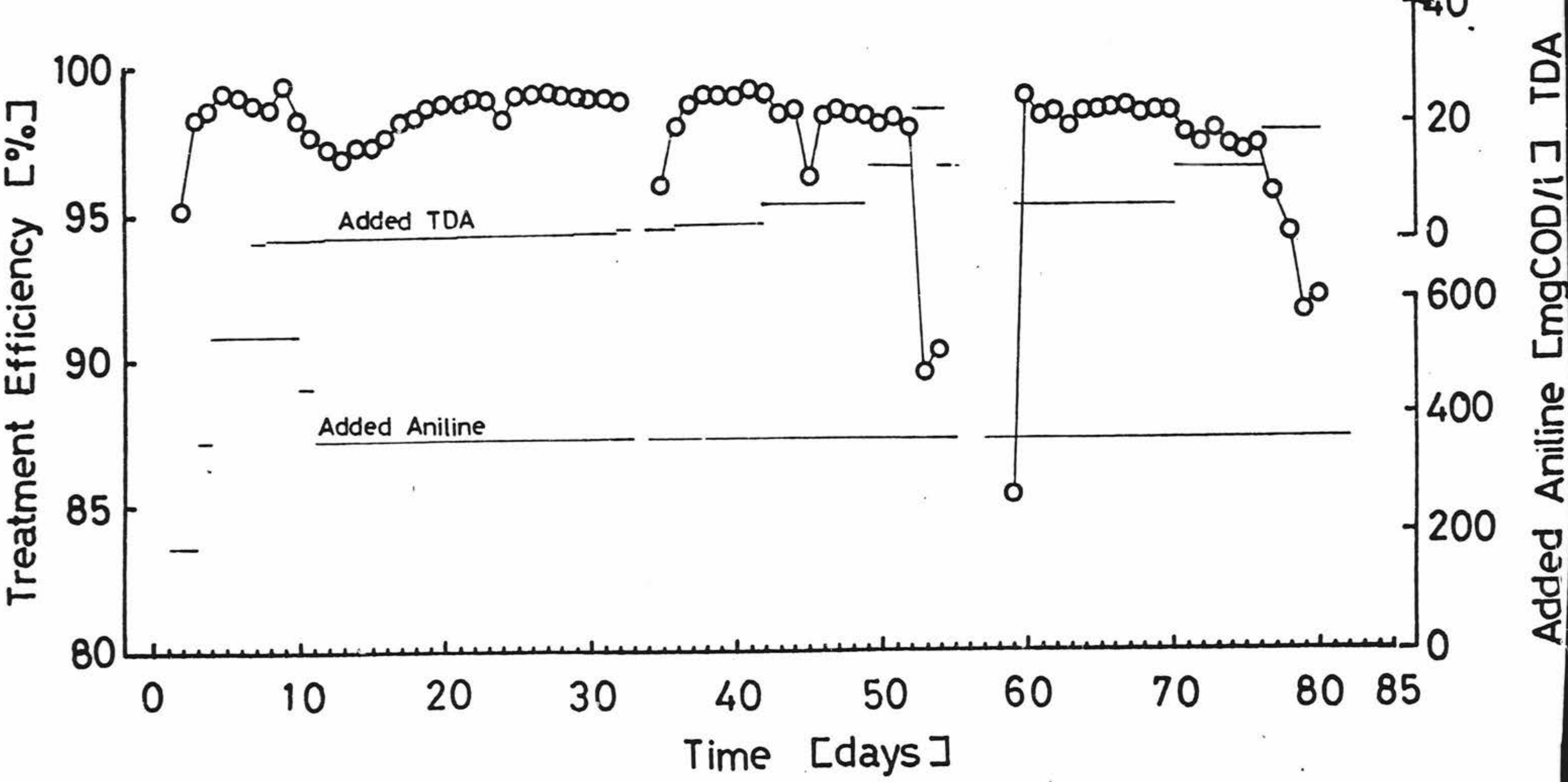


Fig. 5-6 Treatment efficiency for culture (I)

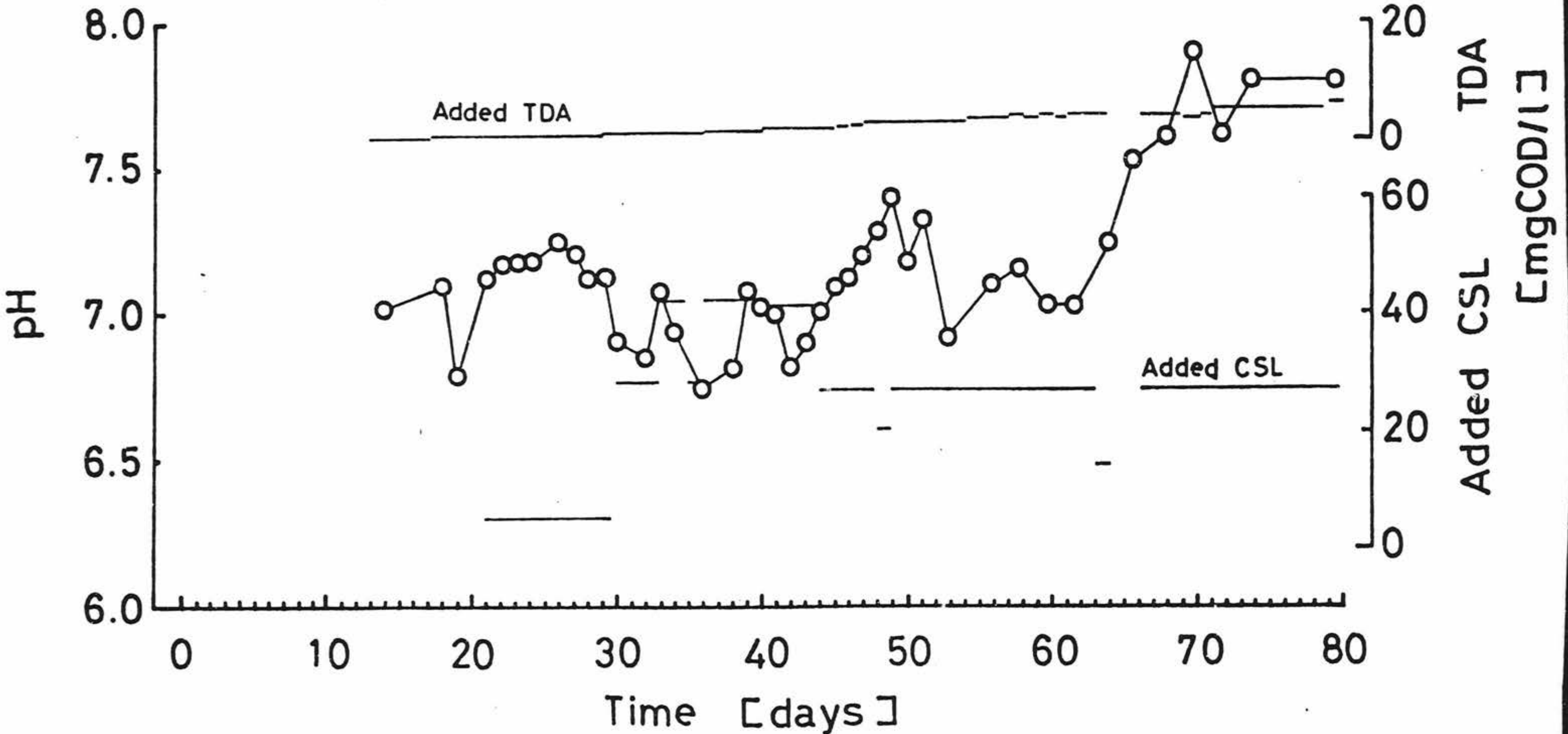


Fig. 5-7 PH change for culture (II)

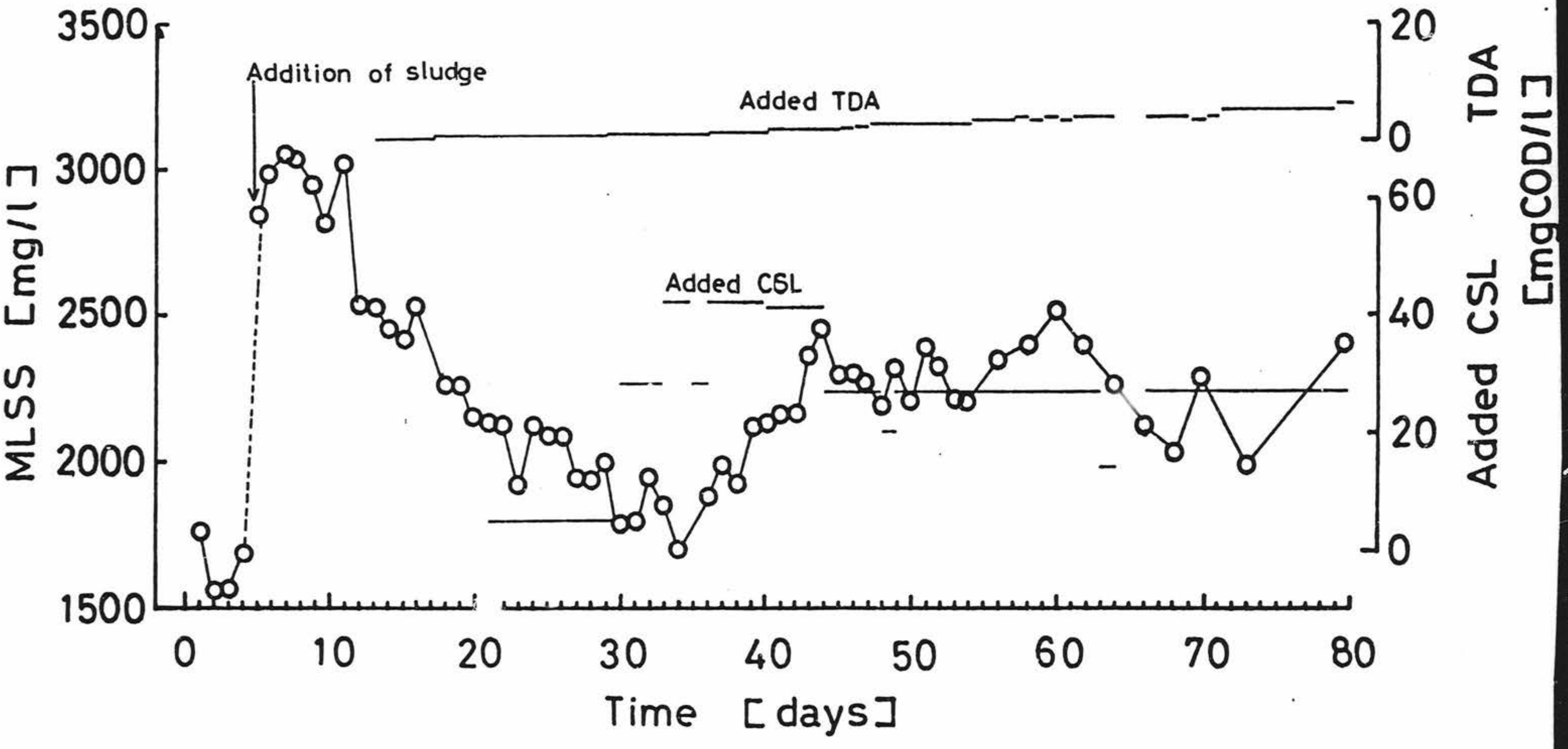


Fig. 5-8 MLSS for culture (II)

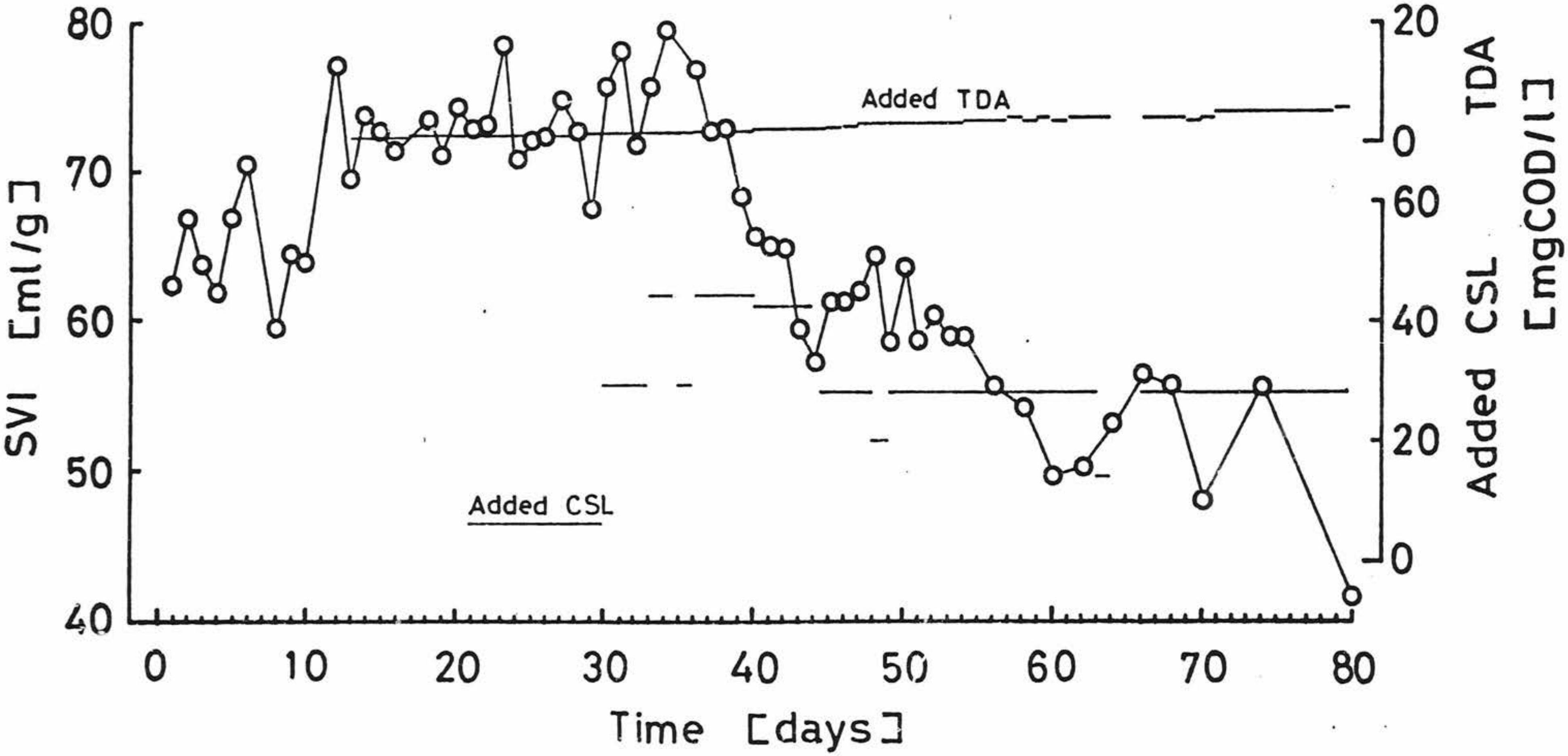


Fig. 5-9 SVI for culture (II)

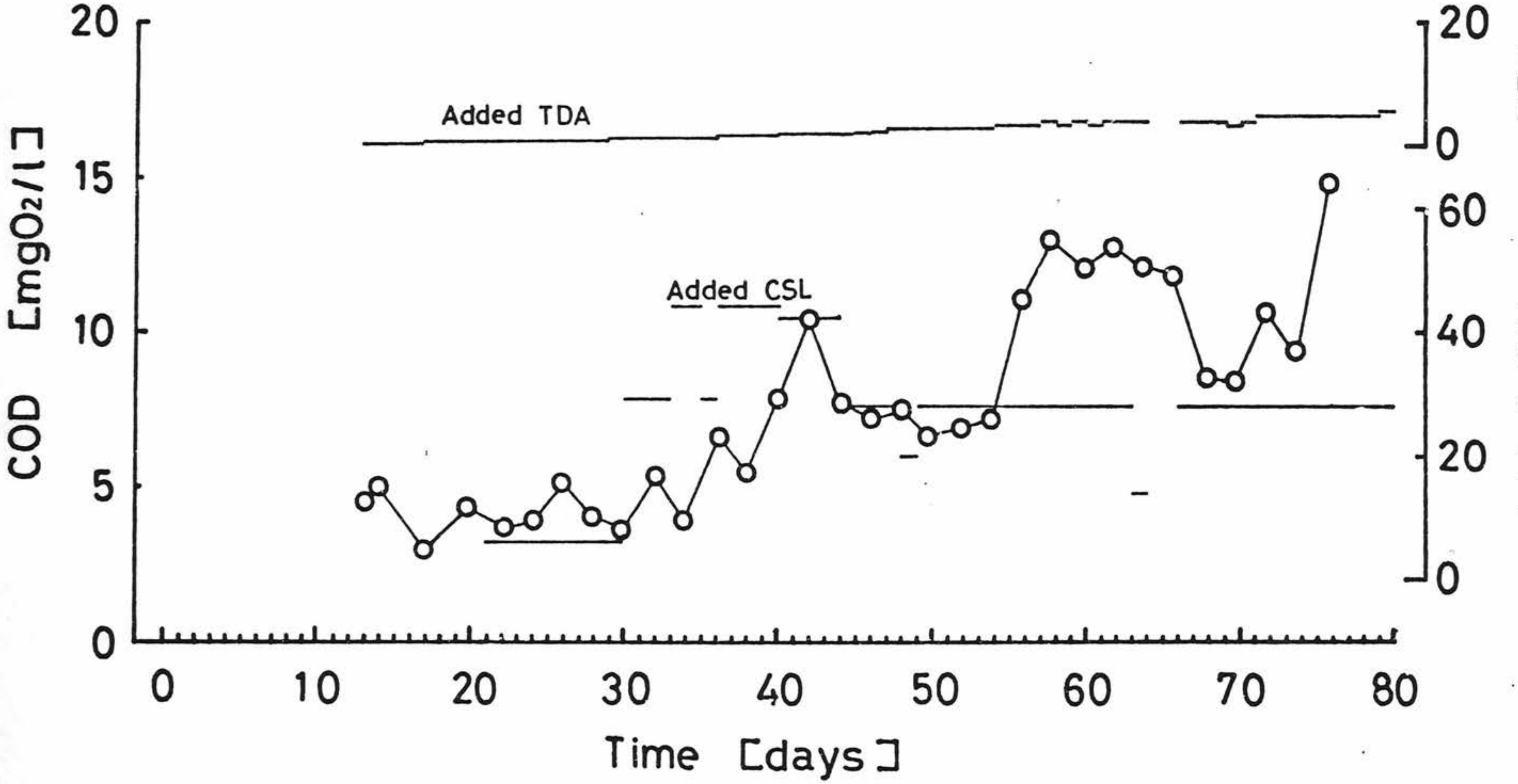


Fig. 5-10 COD of top water for culture (II)

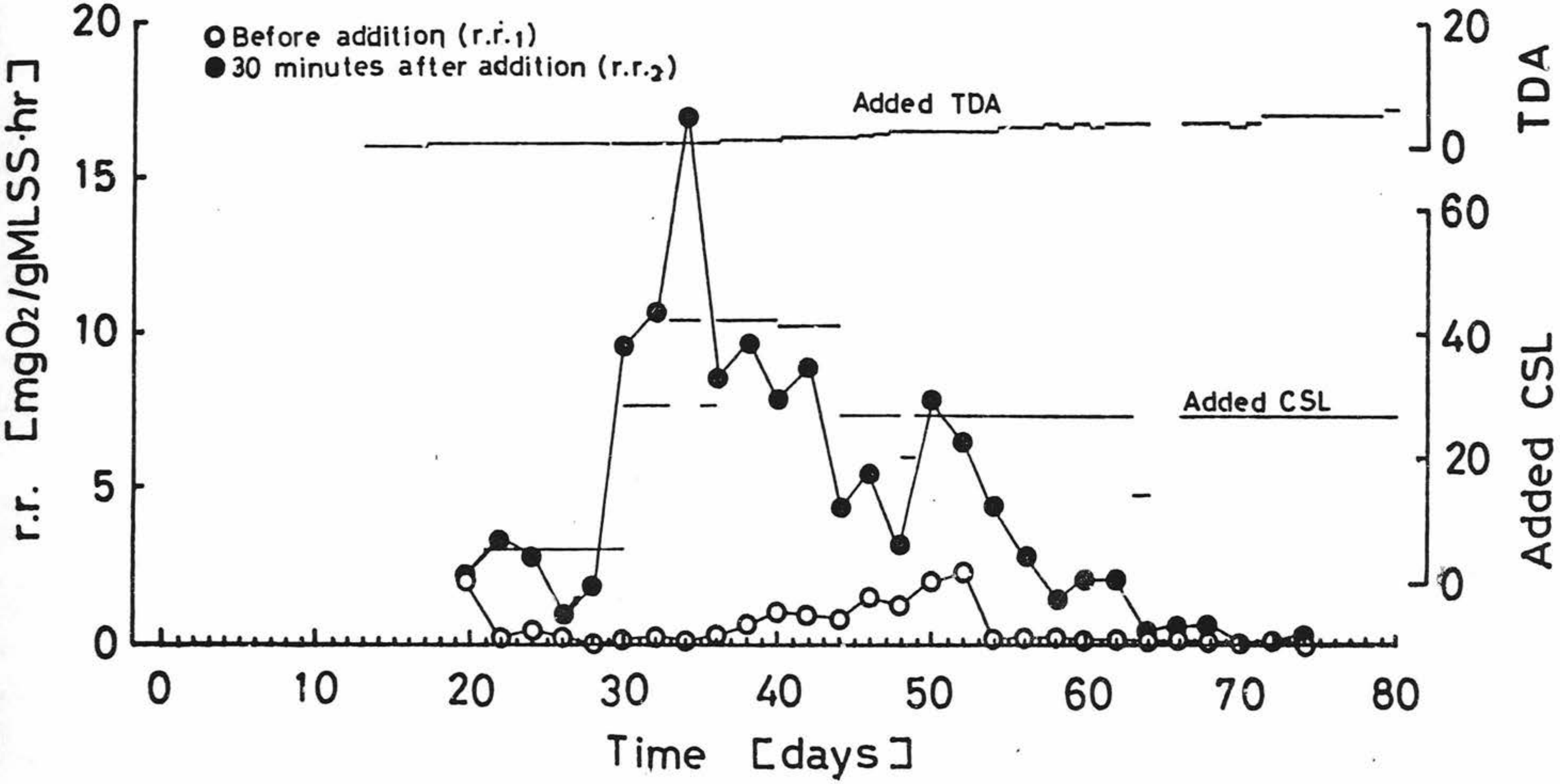


Fig. 5-11 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II)

6. Culture of activated sludge with triethylenediamine

6.1 Introduction

As has been already stated in the previous report (III Project No. FE-E-15) triethylenediamine (TEDA) was soluble into water and enhanced the respiration activity of the activated sludge. However, this enhancement did not always directly indicate that TEDA could be metabolized and assimilated.

In this chapter, the possibility of acclimation of TEDA into activated sludges was examined.

6.2 Experimental

The outline of experimental procedure was same as that of preceeding chapters.
The aniline acclimated and CSL acclimated sludges were stored in the vessels of about 30 ℓ and aerated.
Top water of 18 ℓ was replaced every day with the same amount of buffer solution which was used in the previous experiments.
Simultaneously, a certain amount of TEDA was added.
Initially, the sludge was aerated without feeding for three days. After then, the addition of TEDA started.
The temperature was maintained around 25°C.
The added TEDA was expressed in the apparent concentration in the sludge solution, i.e. it was given by dividing the total amount of COD of added TEDA by entire volume of sludge solution.

6.3 Results for the culture of aniline acclimated sludge with triethylenediamine (Culture I).

The expression for the quantities of added TEDA and aniline was same as that in previous chapters.

6.3.1 pH

pH increased to about 7.7 being accompanied by the concentration of TEDA. (Fig. 6-1)

6.3.2 MLSS

MLSS decreased in the initial period and then stayed at about 1000 mg/ℓ constantly. (Fig. 6-2)

6.3.3 SVI

SVI raised gradually from 50 to 100 mℓ/g. (Fig. 6-3)

6.3.4 COD

COD of Top water before replacing it increased. This was paralleled with the concentration of added TEDA. (Fig. 6-4)

6.3.5 Respiration rates

The respiration rates before the addition of TEDA (rr_1) and after the addition (rr_2) are given 6-5.

rr_1 was almost zero while rr_2 was detectable though the value itself was low.

6.3.6 Visual Observation

The apparent conditions of floc and top water did not alter.

Protozoans was not found.

6.4 Discussions for the culture of aniline acclimated sludge with triethylendiamine (Culture I).

Concerning MLSS and rr_2, the sludge was in the course

of acclimation with TEDA.
The initial decrease in MLSS was followed by the stoppage of the tendency. As already been experienced in the acclimation experiment with aniline, MLSS was reduced in the initial period (Step 1), maintained a constant value for a while (Step 2), and started to increase (Step 3).
The comparison of the present result to that in the case of aniline surmised the possibility of acclimation of TEDA to activated sludge.
This anticipation was supported by the gradual increase of rr_2.
However, the result on COD was not always favourable to this anticipation.
The increased value of COD indicated the possibility that TEDA resided without metabolizing.
This contradiction would be reconciled by assuming the reaction intermediates in the assimilation processes.. It was regretable that the cultural time was too short to obtain the definite conclusion.
In conclusion, though the limited time of experiment made the judgement vague TEDA seemed to be treated with activated sludge.

6.5 Results for the culture of CSL acclimated sludge with triethylendiamine (Culture II).

6.5.1 pH

pH increased with the addition of TEDA. (Fig. 6-6)
This change could be ascribed to the neutralizing effect of TEDA and/or to the alteration of metabolism by its addition which actually meant the inhibition of nitrifying reaction with TEDA.

6.5.2 MLSS

MLSS decreased monotonically with time regardless of the addition of TEDA. (Fig. 6-7)
As its decay seemed to be exponential, logarithm of MLSS was plotted against time as shown in Fig. 6-8. From this plot the relation

$$[MLSS] = K \exp(-kt)$$

or

$$\frac{d[MLSS]}{dt} = -k[MLSS]$$

is obtained, where t is time, K and k are constants. This equation followed the decay relation of MLSS under the endgeneous conditions which had been mentioned in the previous report for III.

6.5.3 COD

COD of top water immediately before its replacement was given in Fig. 6-9. It was jumped up from about 10 ppm to about 100 ppm immediately after the addition of TEDA started. It was noted that the concentration of COD in the top water was higher than that of added TEDA. This indicated that the floc was decomposed to colloidal particle and/or soluble substances by the addition of TEDA.

6.5.4 SV_{30} and SVI

Both SV_{30} and SVI decreased with time as shown in Fig. 6-10. The decrease was accelerated by the addition of TEDA.

6.5.5 Respiration rate

Fig. 6-11 gives the respiration rate immediately after the addition of TEDA. The addition enhanced the respiration rate.

6.5.6 Biological observation

The top water a few days after TEDA started to be added became turbid. Being indicative from the value of SVI so high as 100, the sludge was in the condition of bulking. Accordingly, a large amount of mold fungi was found.

6.6 Discussions for the culture of CSL acclimated sludge with triethylendiamine (Culture II)

The review of whole experiment presented the rather contradictory results such as;

(1) The decrease in MLSS indicated the difficulty in the assimilation of TEDA.

(2) The promotion of respiration rate and reduction of SVI by the addition of TEDA presumed the possibility of metabolism.

(3) The sudden increase in COD of top water surmized the decomposition of floc, i.e. an effect of TEDA on the sludge. The two ways of explanation seemed to be possible.

(1) On the assumption that TEDA was metabolized.

TEDA and/or reaction intermediates loosened the adhesive bond in the floc. The finely divided solid was dispersed into the solution. The particle was divided too finely to settle. Thus, the increase in COD of top water and the decrease in MLSS were resulted.
The decrease in SV_{30} could also be explained

in the same manner.

(2) On the assumption that TEDA was not metabolized.

TEDA was hypothesized to remain unreacted in the solution. being similar to phosphates, TEDA stimulated respiration activity as a by-effect. Also, TEDA promoted the coagulation of suspended solid.

According to author's opinion, the first assumption was more natural because it was hardly presumed that TEDA, an organic substance, provided the effects on metabolic activity without any chemical alteration. The analytical identification of the solution during culture would provide the clear conclusion.

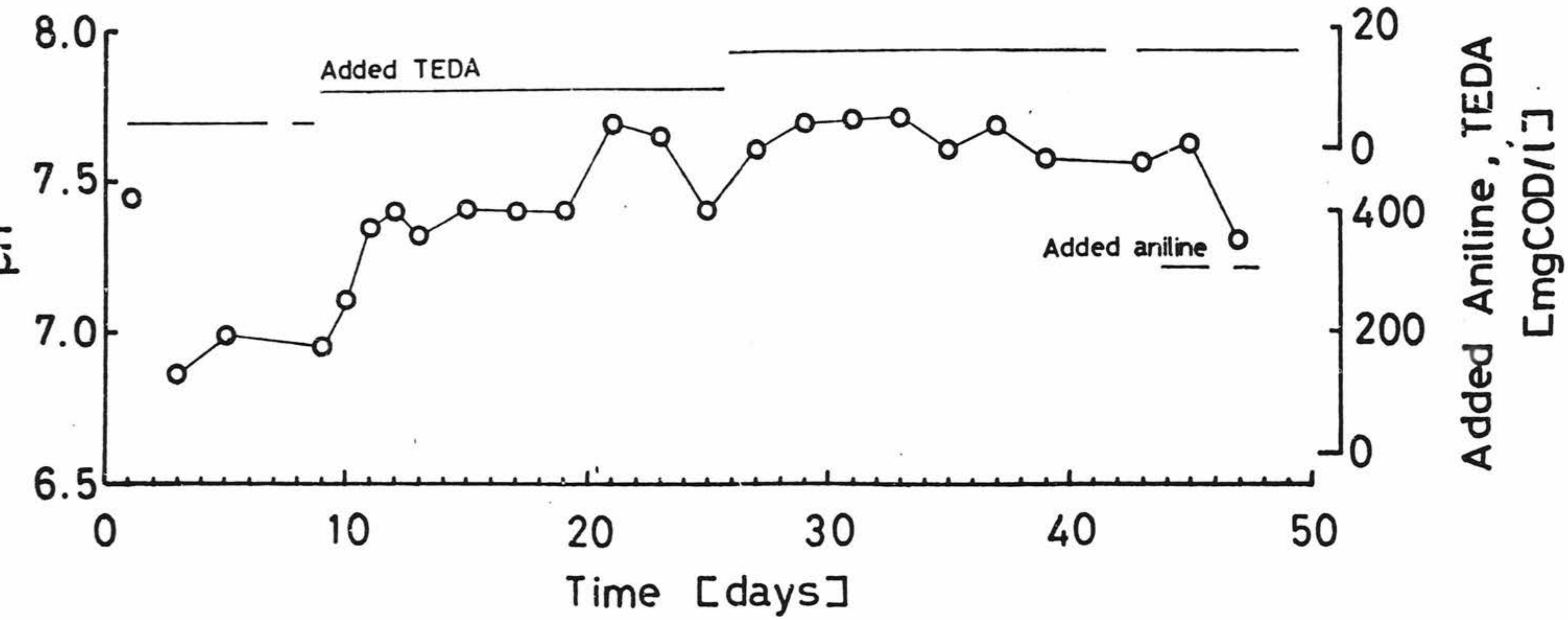


Fig. 6-1 PH change for culture (I)

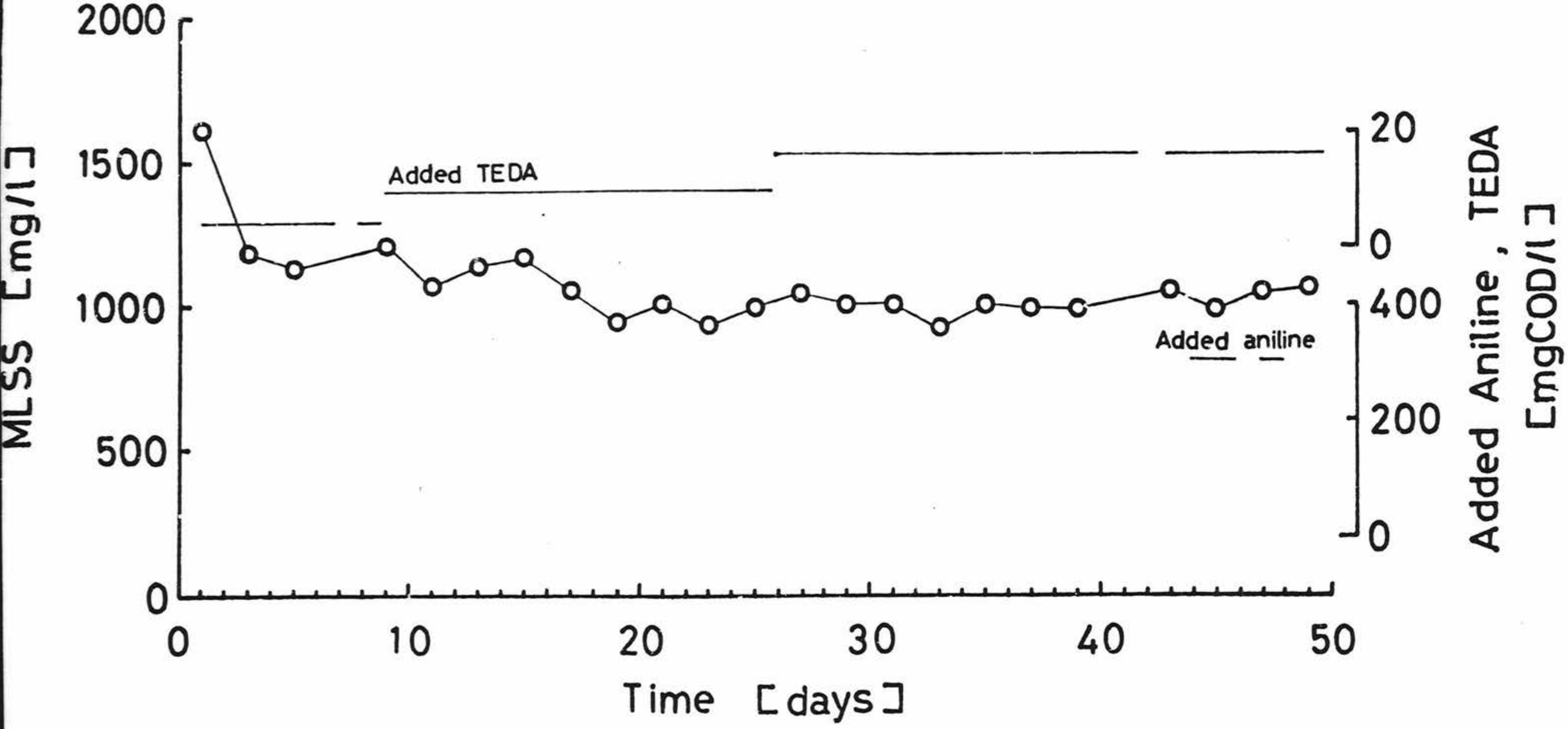


Fig. 6-2 MLSS for culture (I)

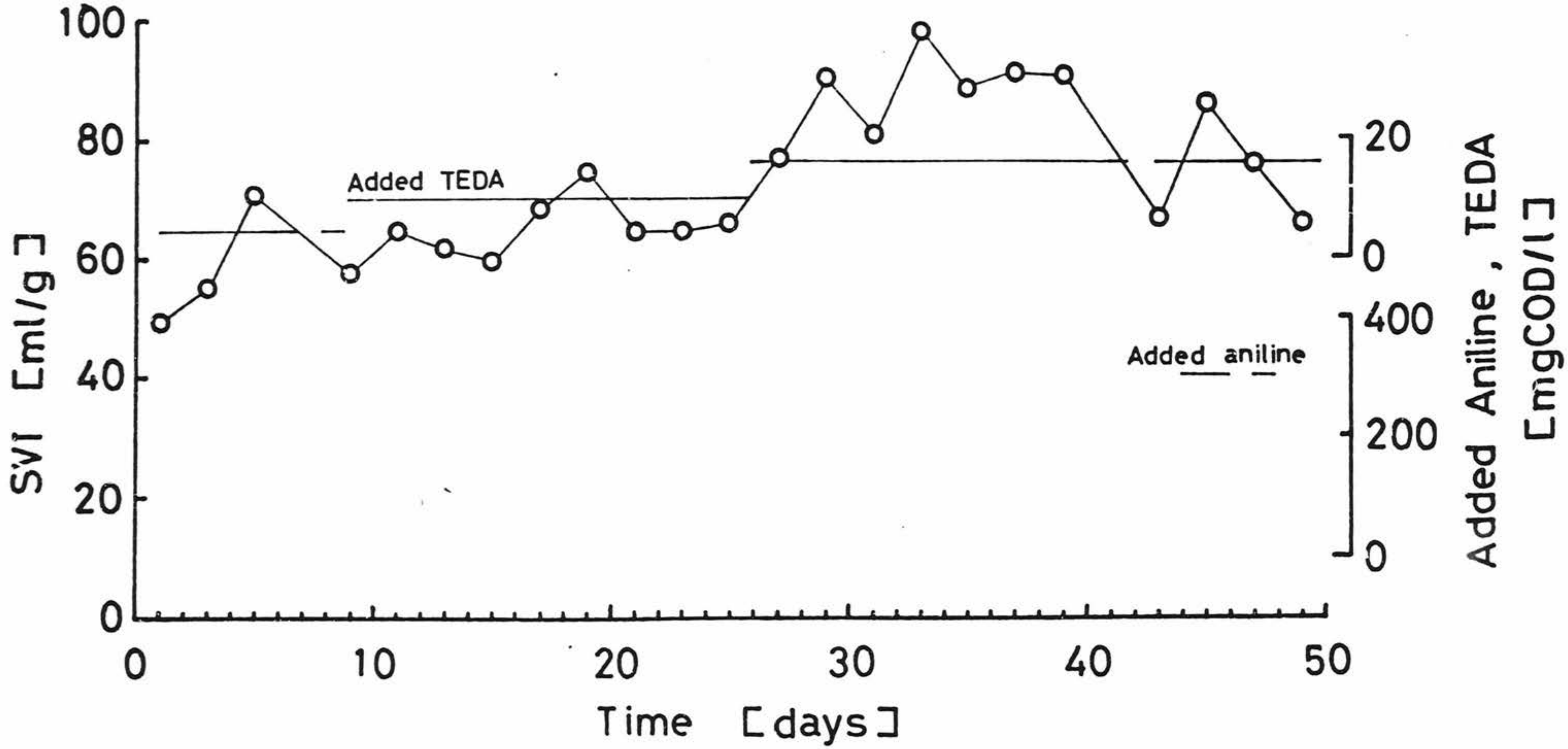
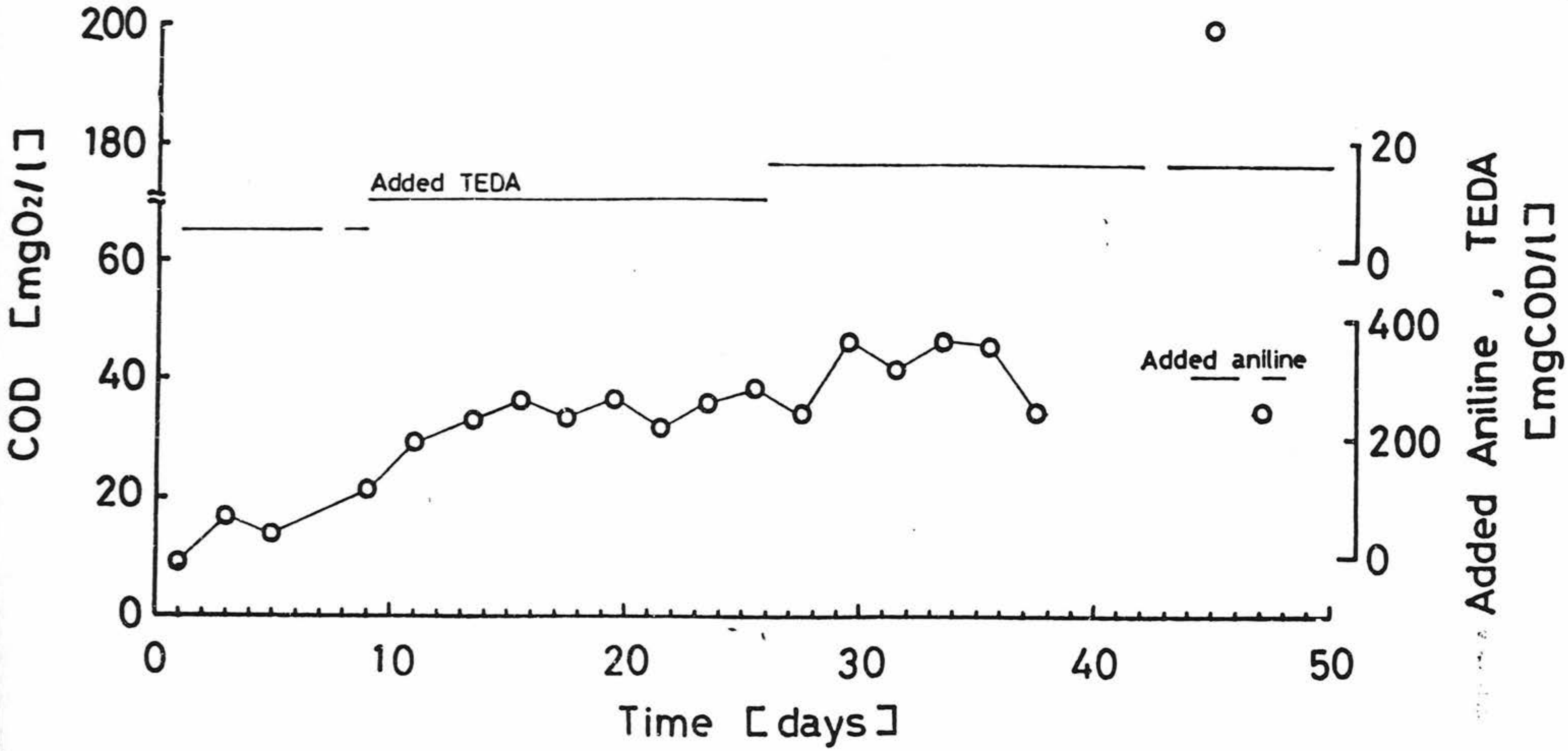


Fig. 6-3 SVI for culture (I)



Fit. 6-4 COD of top water for culture (I)

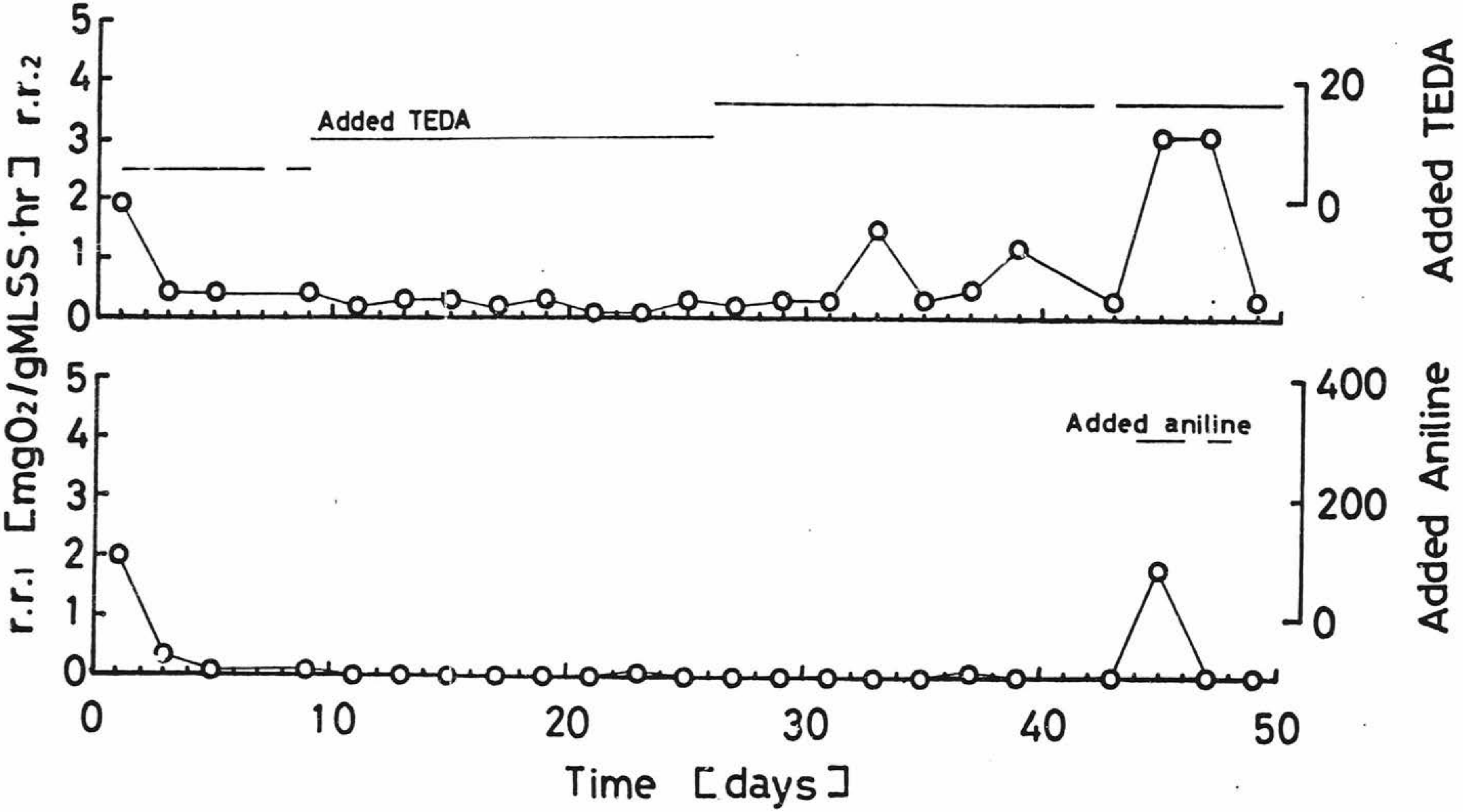


Fig. 6-5 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (I)

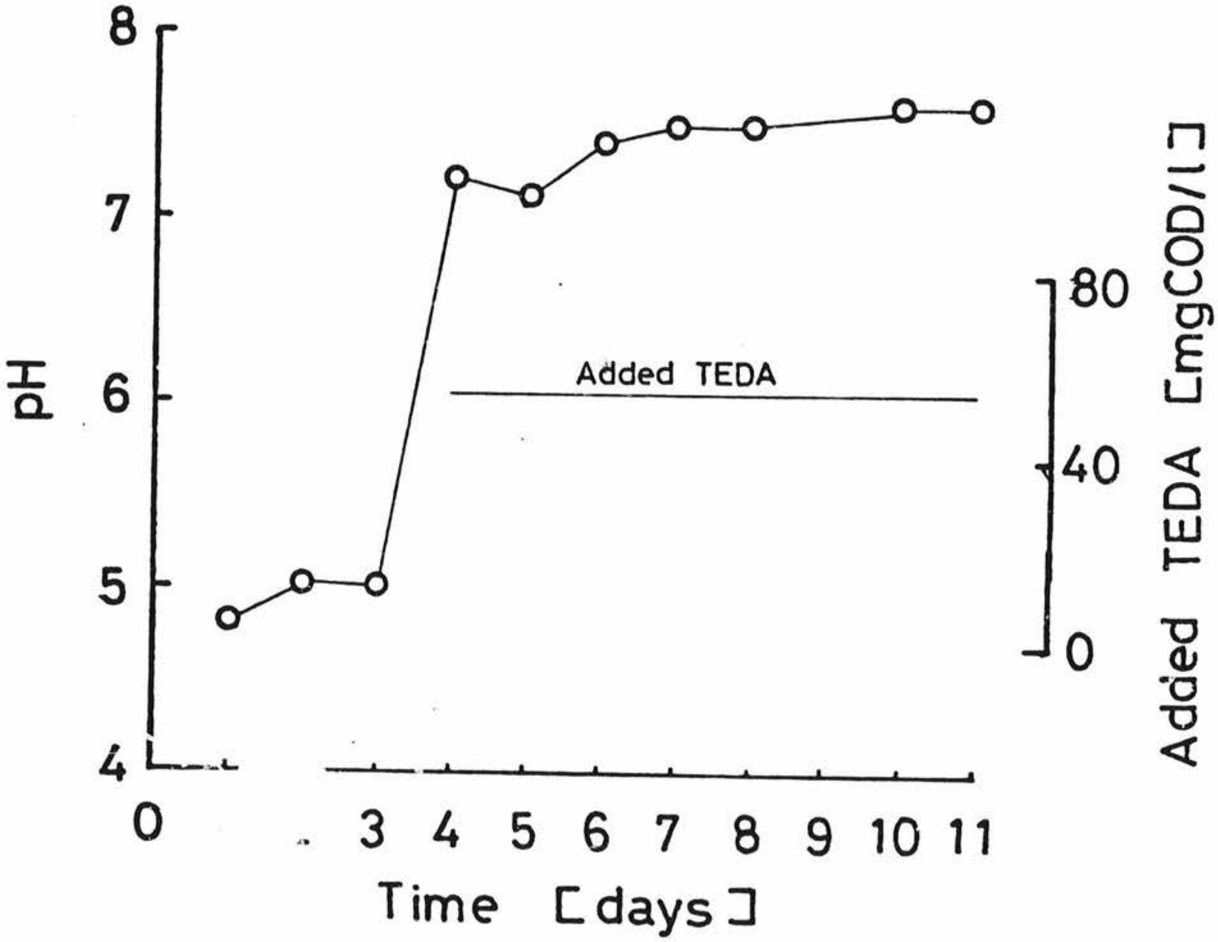


Fig. 6-6 PH change for culture (II)

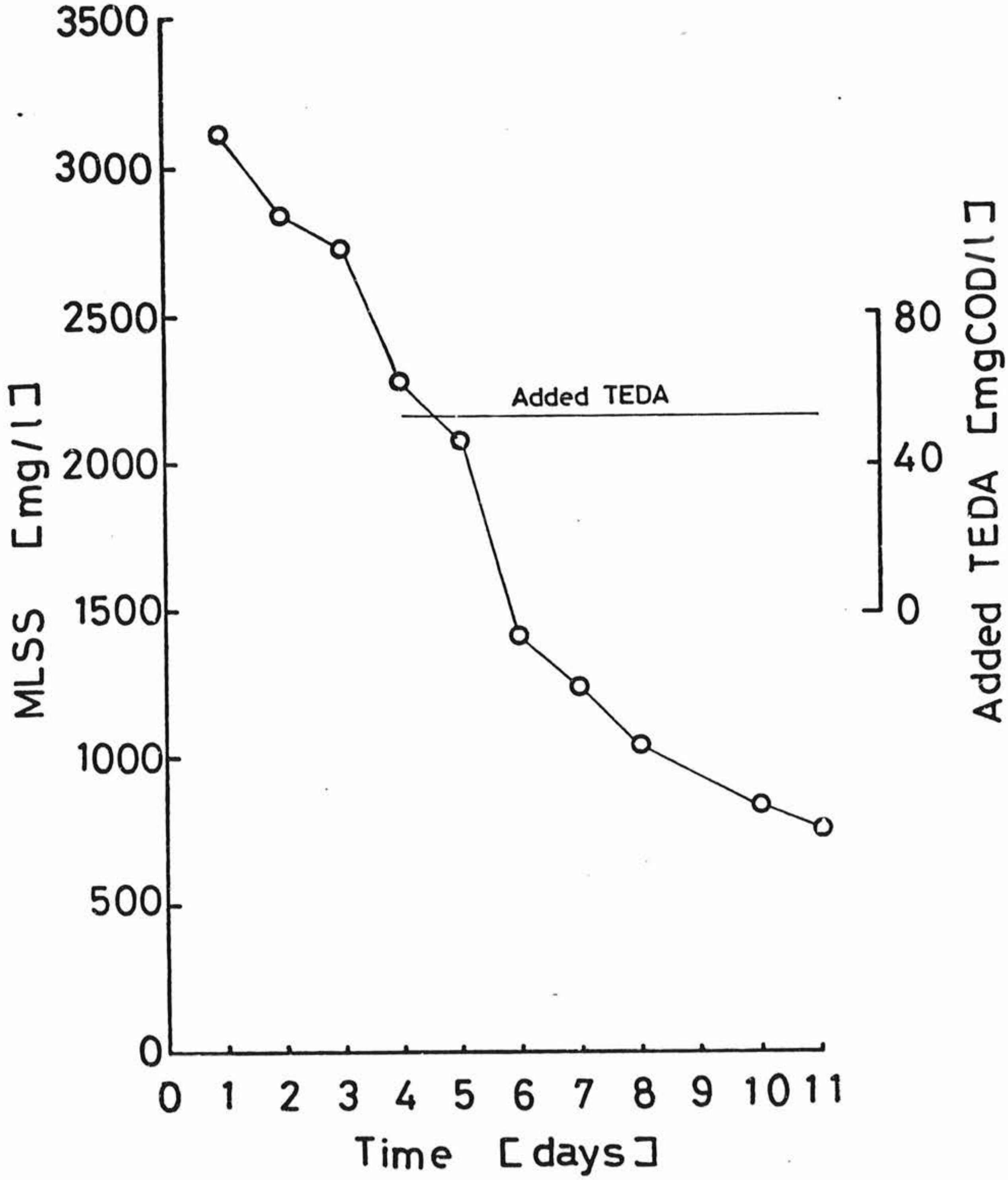


Fig. 6-7 MLSS for culture (II)

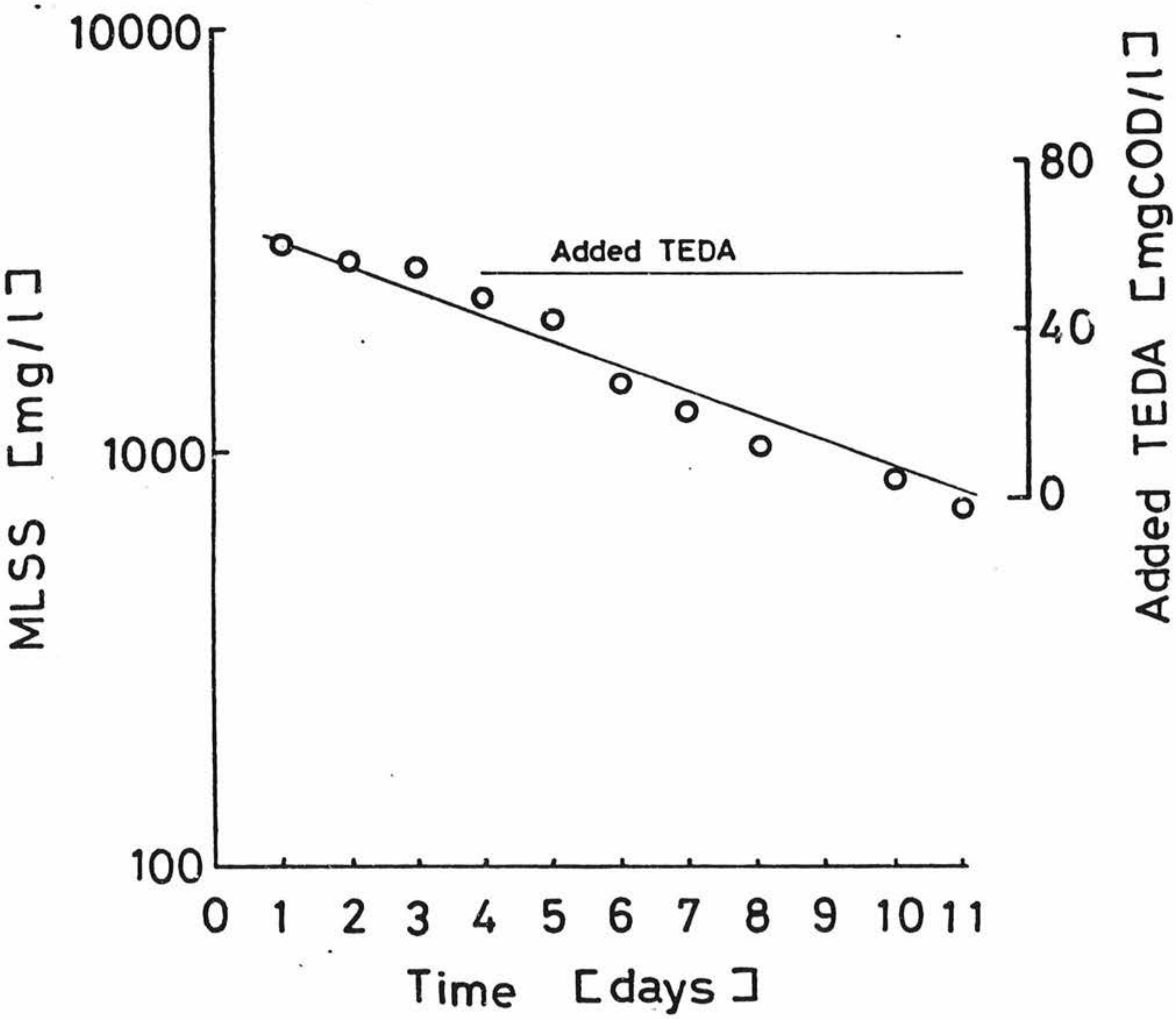


Fig. 6-8 MLSS versus time for culture (II)

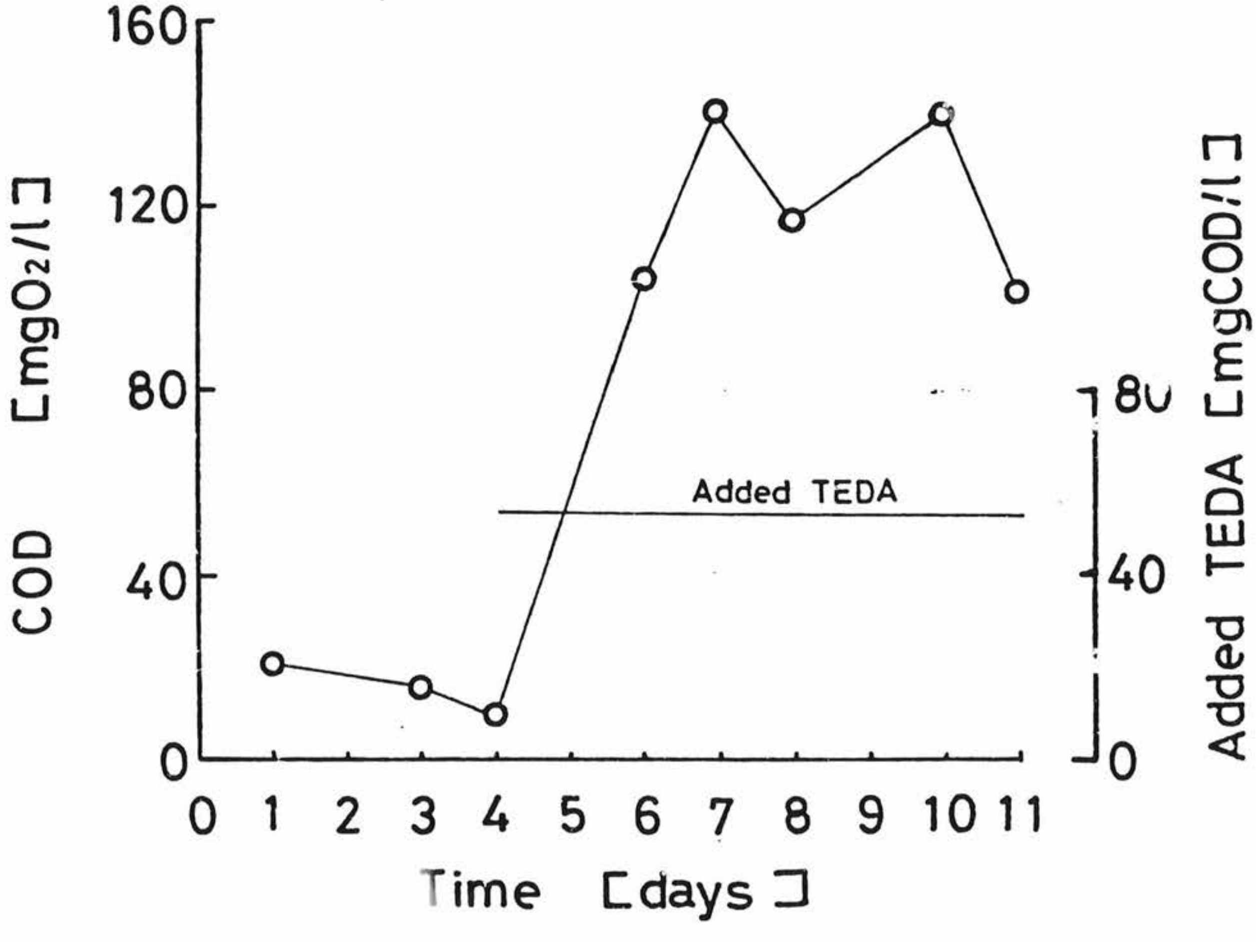


Fig. 6-9 COD of top water for culture (II)

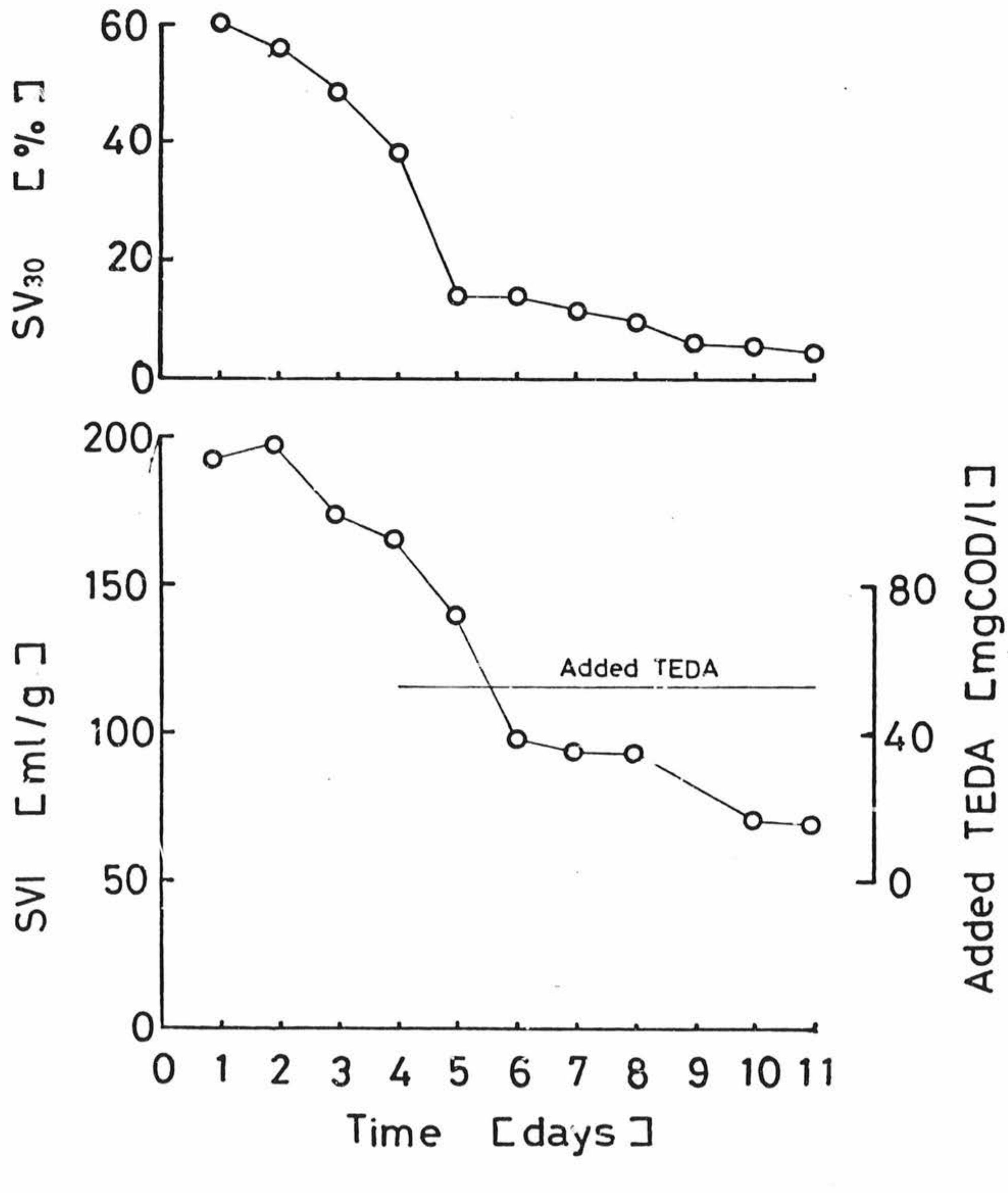


Fig. 6-10 SVI and SV_{30} for culture (II)

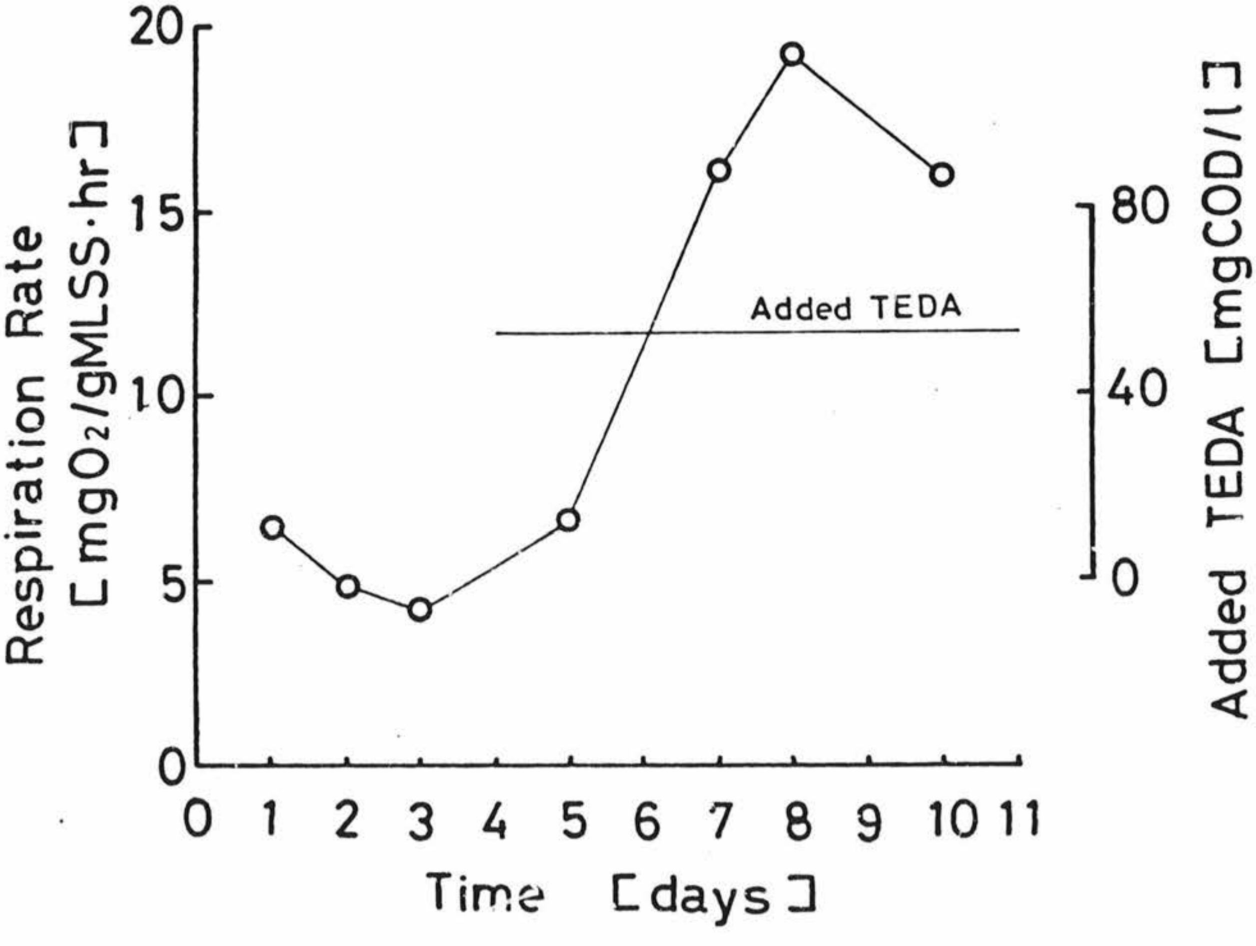


Fig. 6-11 Respiration rate for culture (II)

7. Culture of activated sludge with NNN'N' tetramethyl-diamino-diethyl-ether.

7.1 Introduction

NNN'N' tetramethyl-diamino-diethyl-ether which has commercial name A-1 has been used in the TDI related industry.

NNN'N' tetramethyl-diamino-diethyl-ether (NTDDE) is soluble into water. Then, the waste water from TDI related industry possible contains NTDDE.

In this chapter the effect of NTDDE on the activated sludge and the possibility of its acclimation to the sludge.

7.2 Experimental

The experimental procedures almost followed previous ones. CSL acclimated sludge was used as an original material. The culture was performed in the vessel of about 25 ℓ. Top water of about 18 ℓ was replaced every day with the buffer solution whose composition was mentioned previously. The culture was continued in an aeration condition at 25°C.

7.3 Results

To exclude prolixity, the commercial name of NNN'N' tetramethyl-diamino-diethyl-ether as A-1 was used here. The added A-1 was expressed in terms of the COD concentration, that is, the value appearing in the axi of "Added A-1" was obtained by dividing the amount of COD for added A-1 by the entire volume of sludge solution.

7.3.1 pH

pH became gradually higher with time to about 8. (Fig. 7-1)
After about 20 days, it was at steady state.

7.3.2 MLSS

MLSS decreased initially as shown in Fig. 7-2. After it stayed at about 1900 mg/ℓ for a certain period it started to raise again. This indicated that A-1 was assimilated with the activated sludge.

7.3.3 SVI

Fig. 7-3 showed that SVI which was as high as 130 initially gradually decreased after 25th day. This indicated that the sedimentation was being improved.

7.3.4 COD

Before 22nd day COD of top water immediately before the replacement of solution increased with the concentration of added A-1. (Fig. 7-4)
However, after 25th day COD was kept constant around 40 mg O_2/ℓ inspite of the increase in the concentration of added A-1.
This also indicated that A-1 stated to be metabolized after 25th day.

7.3.5 Respiration rates

The respiration rate immediately before the addition of A-1 (rr_1) was almost nil as shown in Fig. 7-5. The respiration rate immediately after the addition of A-1 (rr_2) was also nil before 30th day. After

then rr_2 began to rise.
This result surmized the possibility of oxidation of A-1 in the latter period.

7.3.6 Visible observations and others

In the initial period a plenty of mold fungi was found, which corresponded to the high value of SVI. As the culture proceeded mold fungi and protozoans disappeared. In the initial period an odor of A-1 was felt in the top water even after 24 hours aeration. However, after 25th day, the odor was not sesible any more.

7.4 Discussions

The following results positively supported the assimilation of A-1 after about 25 days' culture.

(1) Increase in MLSS.

(2) The detectable respiration rate after the addition of A-1.

(3) The stagnation of COD in top water despite the increase in the concentration of added A-1.

(4) The elimination of A-1 odor in top water.

(5) The diminution of SVI.

All of these results resembled those for the case aniline acclimation. Thus, it would be concluded that A-1 could be assimilated and treated with CSI-cultured activated sludge.

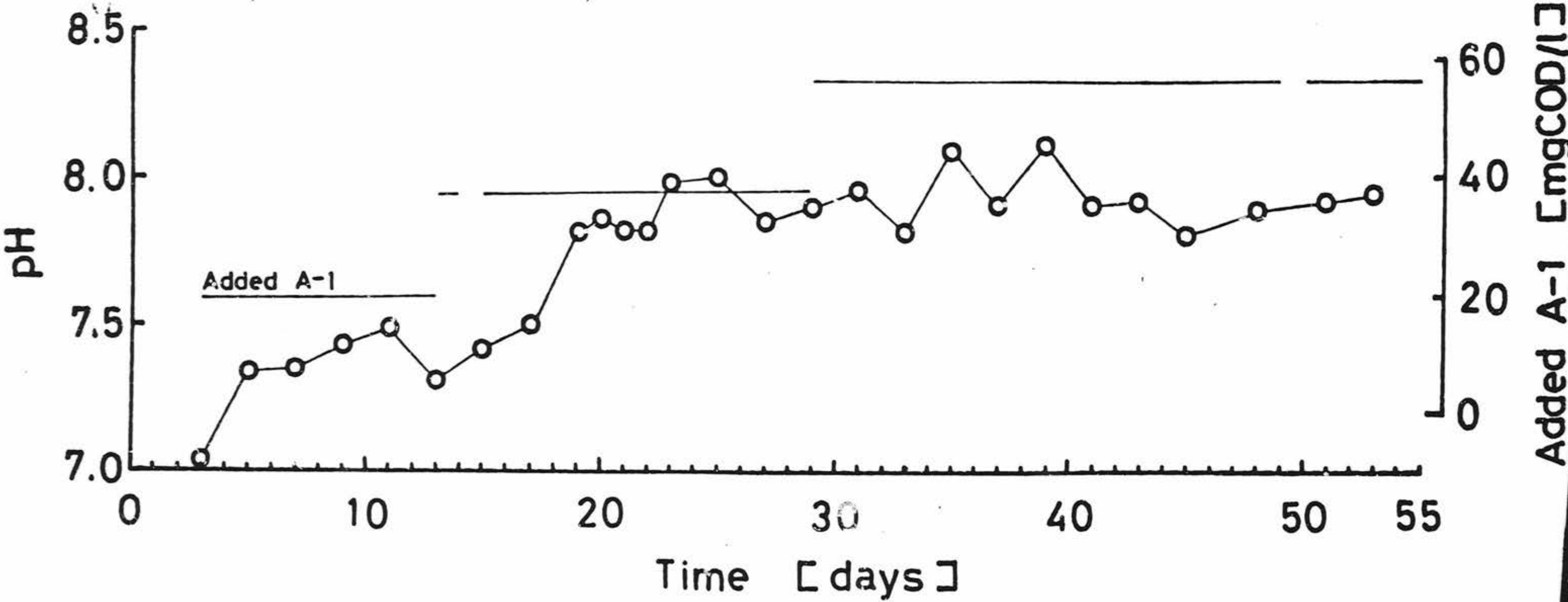


Fig. 7-1 PH change of activated sludge during culture with A-1

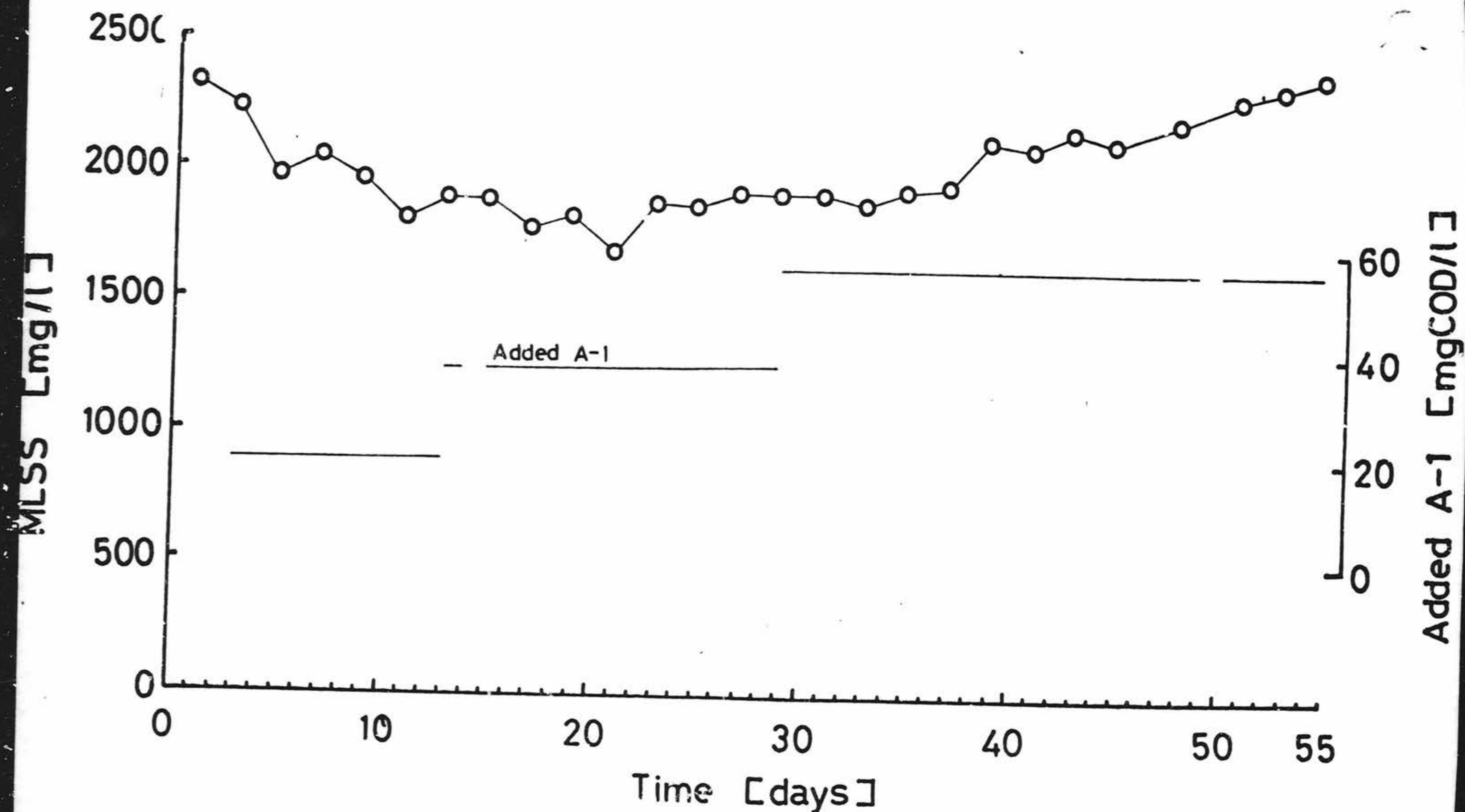


Fig. 7-2 MLSS of activated sludge during culture with A-1

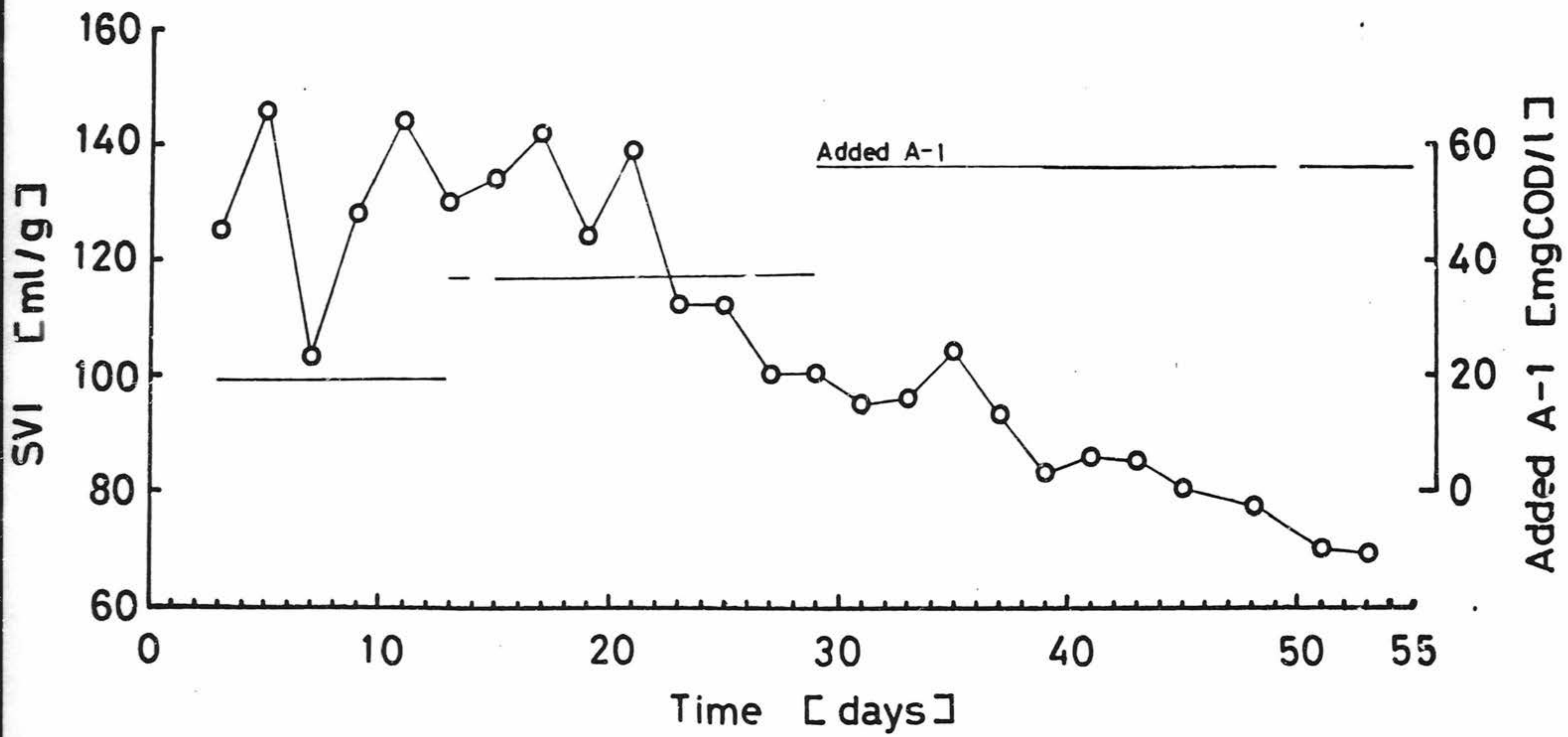


Fig. 7-3 SVI of activated sludge during culture with A-1

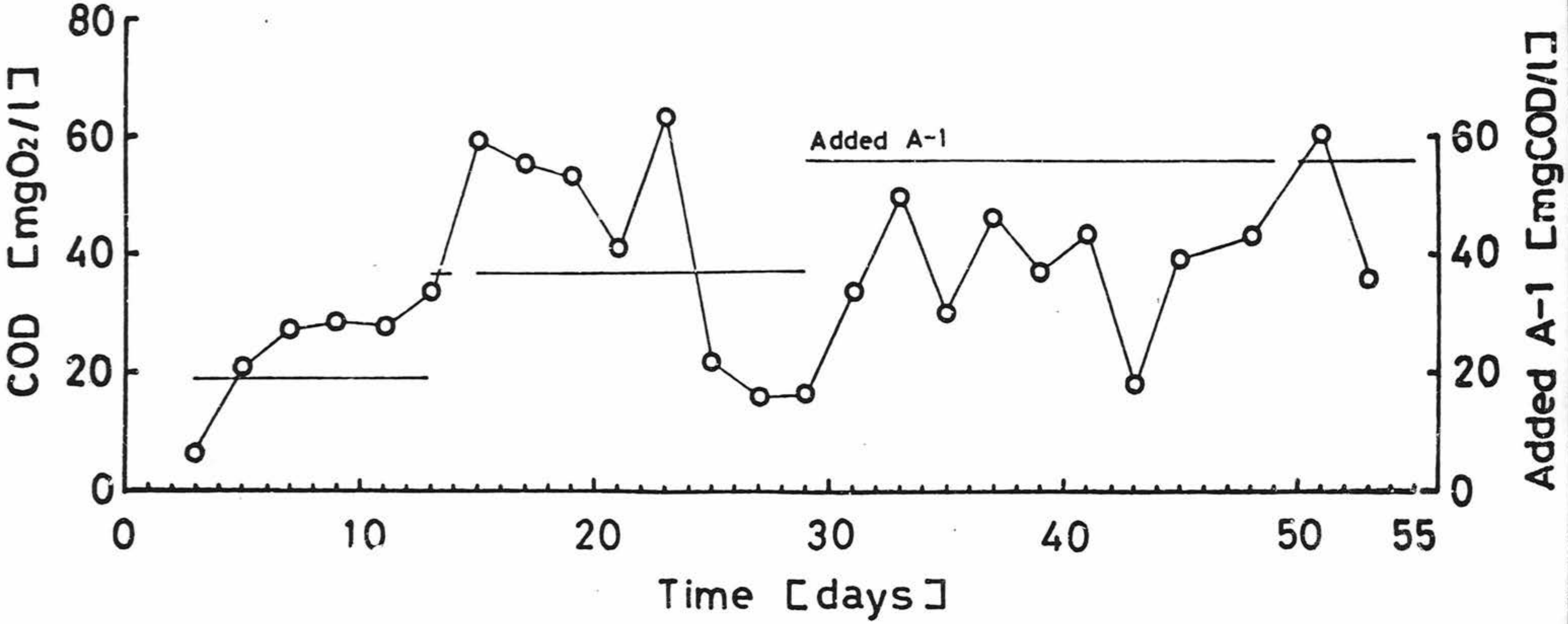


Fig. 7-4 COD of top water during culture with A-1

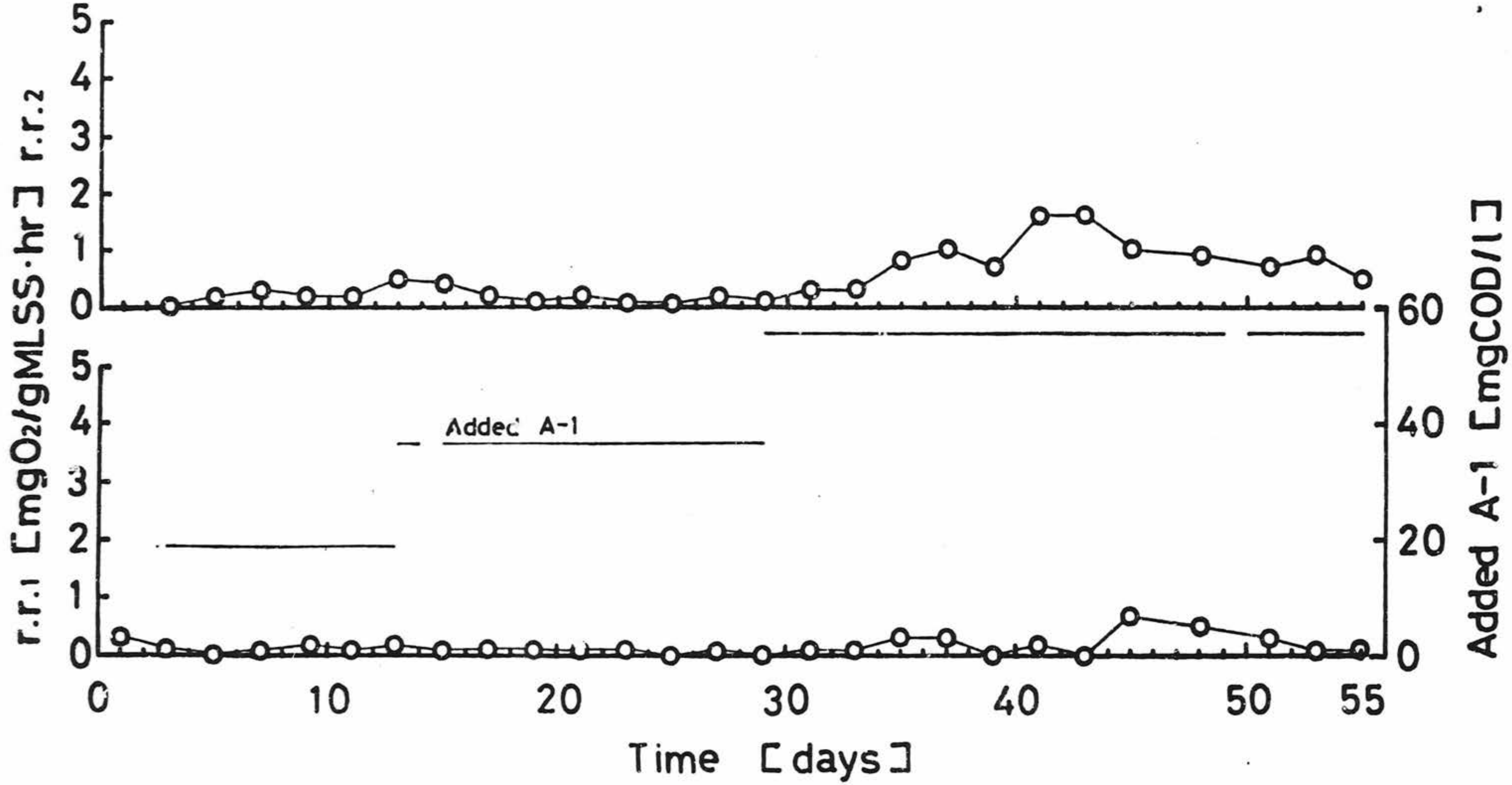


Fig. 7-5 Respiration rates before (r.r.1) and after (r.r.2) the addition of A-1

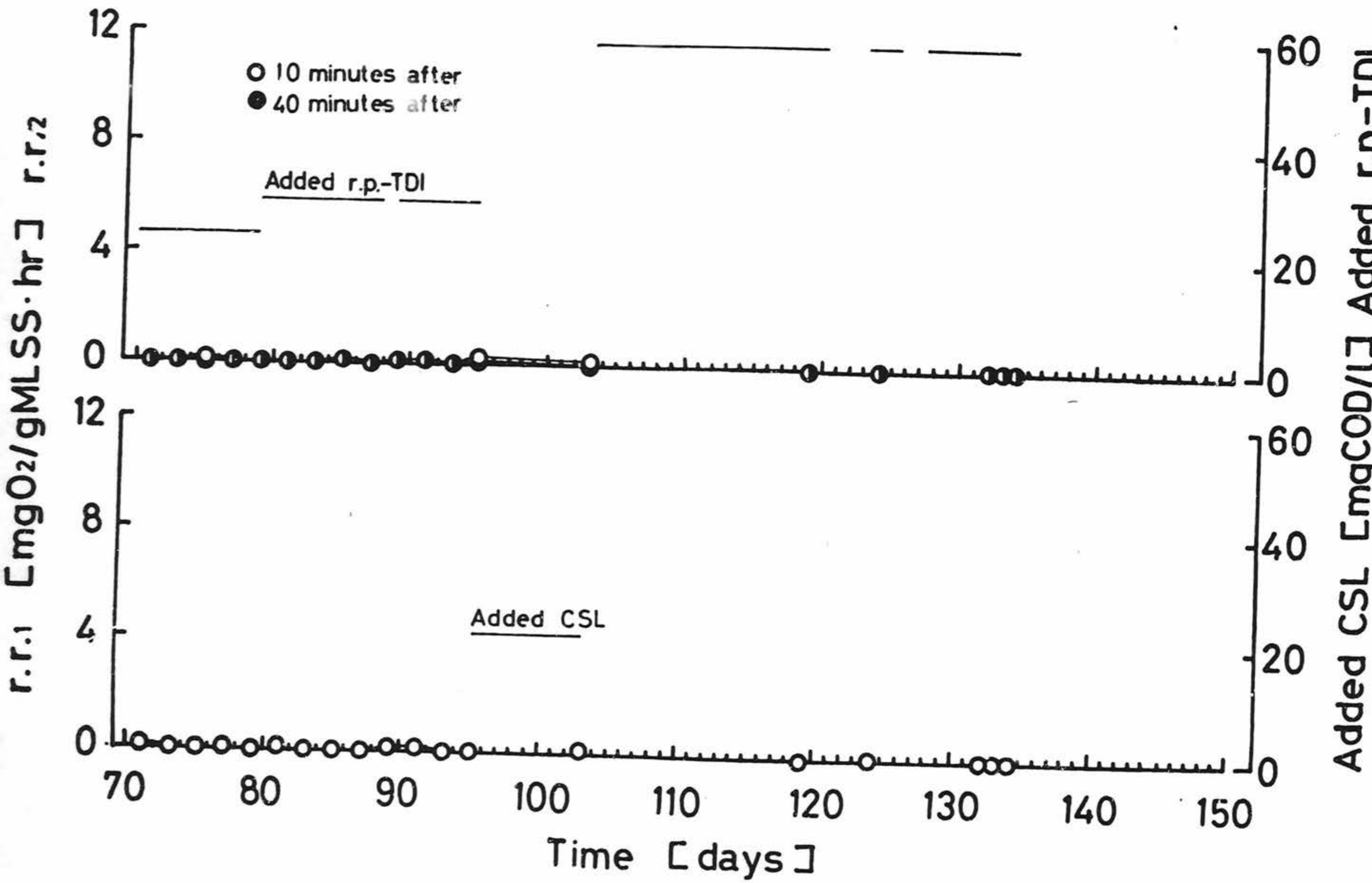


Fig. 4-10 Respiration rates before (r.r.1) and after (r.r.2) the addition of nutritions for culture (II) (2)

CERTIFICATE OF AUTHENTICITY

THIS IS TO CERTIFY that the microimages appearing on this microfiche are accurate and complete reproductions of the records of U.S. Environmental Protection Agency documents as delivered in the regular course of business for microfilming.

Data produced 11 18 88 Barbara Smith

(Month) (Day) (Year) Camera Operator

Place Syracuse New York

(City) (State)

AMTEK corp